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LXIII. *On Reactions in Solids.*

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DESPITE the increased attention which has been paid to the study of solid reactions in recent years, no clear resolution of the factors governing the type of curve representing the course of the reaction has been attempted. In this paper we shall endeavour to investigate the importance of various factors in reactions of the type:—

solid \rightarrow solid

solid \rightarrow solid + gas or liquid.

An example of the former type is found in the change of monoclinic sulphur to rhombic sulphur⁽¹⁾ and of the latter in the decomposition of calcium carbonate hexahydrate⁽²⁾.

These reactions, which consist essentially of the transformation of a metastable crystal lattice into one of greater stability, are characterized by the initiation of reaction at certain points where the formation of an element of the new lattice serves as a nucleus from which the decomposition spreads. From general considerations it appears that the most probable position for nucleus formation is the surface of the solid, particularly at points where deformation has occurred. By observation of the transformation of monoclinic sulphur into rhombic sulphur and of the dehydration

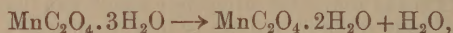
* Communicated by Prof. R. Whytlaw-Gray.

of potassium hydrogen oxalate hemihydrate⁽³⁾, this view has been completely confirmed. Provided that solid solution formation does not occur between the reactant and the resultant, it has been shown by Langmuir⁽⁴⁾ that reaction can take place only at the interface separating the two solid phases. The rate of advance of the interface, which we shall assume to be constant and the same in all directions, we shall call the linear rate of propagation.

The three factors governing the course of the reaction then are :

1. Rate of nucleus formation.
2. Linear rate of propagation.
3. Size of the reactant particles.

Observation of the course of such transformations shows that the formation of nuclei is invariably preceded by a more or less prolonged period of induction, the duration of which is markedly influenced by the previous history of the reactant. Despite this, once the formation of nuclei begins, the velocity of the subsequent reaction appears to be characteristic of the particular preparation. This is clearly demonstrated in the reaction



which can be followed dilatometrically. One portion of a specimen of manganous oxalate trihydrate was placed in a dilatometer under its saturated solution and maintained at $25 \pm 0.1^\circ \text{C}$. Under these conditions reaction was complete in about three hours. A second portion of the same specimen, washed thoroughly in ice-cold distilled water before placing in the dilatometer at the same temperature, showed an induction period lasting more than three days, although once the reaction started, decomposition proceeded as rapidly as before. In some reactions, especially those with a large rate of nucleus formation, this induction period is negligible. In this case, if the rate of nucleus formation is very great relative to the linear rate of propagation, the particles of the reactant will become covered instantaneously with a layer of resultant of approximately uniform thickness. Assuming the particles to be spherical, the volume of resultant v formed in the time t seconds after the beginning of the reaction will be given by the expression

$$v = \frac{4}{3} \pi a^3 - \frac{4}{3} \pi (a - ut)^3,$$

where u is the linear rate of propagation in cm./sec., and a is the radius of the particle in cm.

Hence the fraction α decomposed in this time will be given by the expression,

$$\alpha = 3\left(\frac{ut}{a}\right) - 3\left(\frac{ut}{a}\right)^2 + \left(\frac{ut}{a}\right)^3. \quad \dots \quad (\text{I.})$$

Clearly the maximum velocity is attained at the beginning of the reaction, since the area of the interface then possesses its maximum value.

On the other hand, the rate of nucleus formation may be such that the particle develops only a small number of nuclei before its decomposition is complete, that is to say, before the interface has time to travel completely across the particle. By assuming that the reactant consists of spheres of uniform size and that each sphere develops only one nucleus, all the nuclei being formed simultaneously, Topley and Hume⁽²⁾ have shown that the fraction α decomposed in time t is given by the expression,

$$\alpha = \frac{1}{2}\left(\frac{ut}{a}\right)^3 - \frac{3}{16}\left(\frac{ut}{a}\right)^4. \quad \dots \quad (\text{II.})$$

By plotting α against t the sigmoid curve associated with autocatalytic reactions results. Hence by suitable choice of the size of particle used, either of the curves corresponding to expressions (I.) or (II.) might be produced. Whether this is possible in practice in a given case will depend on the relative velocities of nucleus formation and of linear propagation.

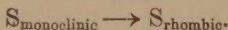
Finally, if the linear rate of propagation is so great that a particle may be regarded as completely decomposed as soon as it develops a nucleus, a new type of curve results. Provided that infection of the undecomposed particles by those already decomposed does not occur, the rate of decomposition will be simply proportional to the rate of nucleus formation, *i. e.*

$$\text{rate of decomposition} = k_0 N_t, \quad \dots \quad (\text{III.})$$

where k_0 is the number of nuclei forming per second, and N_t the number of undecomposed particles present at time t . From this it follows that the reaction will be pseudo-monomolecular and should give a first-order velocity constant. Moreover, since the conditions for the applicability of equation (III.) will be best fulfilled by small particles, the course of all reactions of the type under consideration should tend to become pseudo-monomolecular by reducing the particle size. Naturally in many cases the

rates of nucleus formation and of propagation may not be consistent with the complete realization of the necessary conditions.

In order to test the views expressed in the preceding section, the following experiments were carried out. The reaction studied is the change



Experimental.

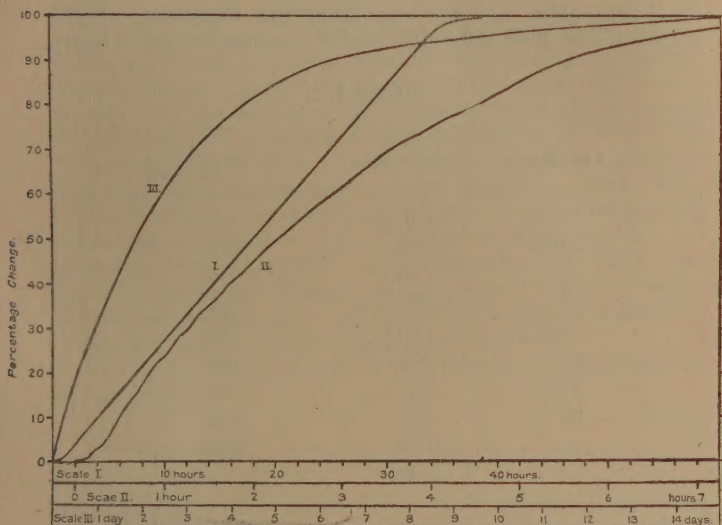
A quantity of rhombic sulphur was converted into monoclinic by heating to 150°C. for two hours. While molten it was poured into the bulb of a dilatometer of the type described by Hume and Topley⁽⁶⁾ and allowed to cool very slowly. When the sulphur had solidified and cooled, air-free distilled water was introduced into the dilatometer. Complete filling of the bulb with water was ensured by repeated evacuation, after which the ground-glass stopper carrying the capillary tube was inserted. The bulb was then immersed in a thermostat maintained at a temperature of $20 \pm 0.2^{\circ}\text{C.}$ The course of the reaction, which is accompanied by diminution in volume, was followed by reading the height of the water-column in the capillary tube.

Curve I. shows the result of plotting the decrease in height of the column calculated as a percentage of the total decrease against the time. The change was seen to begin on the free surface of the sulphur and to spread outwards across the surface. This gives rise to the initial autocatalytic portion of the curve. When spreading had occurred across the whole free surface the interface then travelled down the tube, giving rise to the long straight portion of the curve. When the rounded end of the bulb was reached, the reaction speed decreased as the interface diminished in area. The whole curve is a special case of the sigmoid curve, having an abnormally long straight portion, owing to the elongated cylindrical shape of the mass of reactant.

In another experiment about two grams of sulphur were fused and, while liquid, distributed in thirty-five approximately circular spots of equal radius on a small glass plate. The plate was then heated to 150° for two hours and cooled slowly. It was then placed in a dilatometer filled with water and immersed in a thermostat at $25 \pm 0.2^{\circ}$, the reaction being followed as before. Curve II. gives the result of this experiment, plotted as before. It will be noted that the curve, more particularly at the start, is made up of small sigmoid portions, which represent the change of individual spots.

The curve up to 10 per cent. decomposition is typically sigmoid; but thereafter approximates to the type of which curve III. is an example.

In a third experiment, a mass of monoclinic sulphur was prepared as before and ground in an agate mortar to a very fine powder. The powder was then introduced into the bulb of a dilatometer, which was filled with water, and maintained at $20 \pm 0.2^\circ$. The course of the reaction is shown in curve III.



Proof that this is a truly monomolecular curve is afforded by the calculation of the velocity constant by the expression

$$k = \frac{1}{t} \log_{10} \frac{\Delta h_0}{\Delta h_0 - \Delta h_t},$$

where Δh_0 is the total contraction of the water column, and Δh_t is the contraction after time t . The results of the calculation are given in the third column of Table I.

The constancy of the values of k is satisfactory, excluding the two earliest points.

For this reaction, therefore, the predictions of the various forms of reaction curve obtainable by altering the size of the particles of the reactant are completely confirmed by an experimental study of the change.

The nature of the phenomena encountered in the investigation of the dissociation of the metallic carbonates, extensively studied by Centnerszwer and co-workers, may be interpreted in terms of the theory outlined. In the reaction,



in the neighbourhood of the dissociation temperature, Centnerszwer and Bružs⁽⁵⁾ found that the velocity of decomposition of freshly prepared cadmium carbonate passed through a maximum after 380 minutes from the beginning of the reaction, and that after this period monomolecular velocity

TABLE I.

t in days.	Δh_t in cm.	$k = \frac{1}{t} \log \frac{\Delta h_0}{\Delta h_0 - \Delta h_t}$
0.0	0.0	
0.03	0.06	.2533
0.13	0.24	.2393
0.71	0.82	.1644
2.10	1.90	.1632
3.0	2.36	.1642
4.0	2.71	.1638
5.0	2.95	.1635
5.8	3.09	.1639
∞	3.48	—

constants were obtained. Samples of cadmium carbonate which had been previously partially decomposed did not show this induction period; but decomposed from the start according to the monomolecular law. From these observations Centnerszwer and Bružs suggested that cadmium carbonate exists in two forms; one of which, the α -form, existing at ordinary temperatures does not dissociate, but at the temperature of the experiment—376°—passes irreversibly into the β -form, which then dissociates into cadmium oxide and carbon dioxide. Comparison of results obtained when dealing with powdered cadmium carbonate with those obtained with the same material pressed into cylindrical form led the authors to conclude that the reaction is independent of the free surface and that reaction proceeds simultaneously throughout the whole mass of reactant, analogous to reaction in the homogeneous gaseous or liquid phases.

This last conclusion is of special interest in that it is in direct opposition to the views of Langmuir⁽⁴⁾ on the analogous reaction, the dissociation of calcium carbonate. If we assume that the dissociation of cadmium carbonate occurs at the interface separating the two solid phases, CdCO_3 and CdO , and there does not appear to be any real evidence to show that such is not the case, an alternative explanation can be offered of the experimental results summarized above, without the necessity of postulating the existence of two forms of cadmium carbonate.

The sigmoid curve obtained for the course of the decomposition of fresh cadmium carbonate by plotting percentage decomposition against time, shows that the maximum velocity occurs when the reaction has proceeded to an extent of only 12 per cent. We conclude, therefore, that the rate of nucleus formation is high relative to the linear rate of propagation, and that consequently the particles become covered with a layer of cadmium oxide, the subsequent reaction proceeding according to equation (I.). This offers a satisfactory explanation of the observation of Centnerszwer and Bružs that partially decomposed cadmium carbonate showed no induction period, in that in the partial decomposition, the particles would develop a complete envelope of resultant.

Moreover, the constancy of the values of k , calculated by the expression

$$k = \frac{1}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t},$$

after the induction period, is not sufficient to disprove the interfacial nature of the reaction. Since no data are given for the size of the particle employed, it is impossible to attempt any complete quantitative treatment of the results. By applying equation (I.), viz.,

$$100\alpha = \left\{ 3\left(\frac{ut}{a}\right) - 3\left(\frac{ut}{a}\right)^2 + \left(\frac{ut}{a}\right)^3 \right\} 100,$$

constant values for the ratio u/a should be obtained for any given run, provided that the reaction proceeds in the way suggested. Table II. contains the results of this calculation for the data of Centnerszwer and Bružs for the decomposition at 376°C .

The constancy of the ratio u/a is sufficient to justify the belief that the reaction is interfacial in nature. If the calculation of u/a is extended to the later stages of the run, it is found that the ratio shows a progressive diminution. This

is to be explained by the earlier extinction of the smaller particles present.

Finally, with reference to the effect of compressing the powdered cadmium carbonate into cylindrical masses, no great change in the behaviour is to be anticipated since mechanical compression would not result in the formation of larger aggregates possessing a continuous lattice.

TABLE II.

Time in min.	Vol of CO ₂ in c.c.	100 α .	$k = \frac{1}{t} \ln \frac{V_{\infty}}{V_{\infty} - V_t}$	u/a .
0	0	0	—	—
40	4.80	3.13	0.000789	0.000262
80	9.59	6.25	0.000809	0.000262
120	14.45	9.42	0.000825	0.000265
160	18.95	12.36	0.000826	0.000262
200	23.44	15.28	0.000828	0.000267
∞	153.4	100.0	—	—

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LXIV. *The Viscosity of Vapours.*—Part I. *Influence of Molecular Association on the Viscosity of Acetic Acid.*
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SUTHERLAND'S formula, which in most cases agrees admirably with the experimental data for gaseous viscosity, almost always fails at low temperatures, and in particular in the range of temperatures below the critical, where the experimental values are usually higher than the

* Communicated by Prof. T. Martin Lowry, F.R.S.

calculated ones. It is natural to attribute this to the non-ideality of the gas, and to introduce corrections based on van der Waals's equation, or on modifications of this equation such as those of van Laar and of Trautz⁽¹⁾; but these corrections would increase the viscosity values⁽²⁾, thus giving still greater divergence from Sutherland's theoretical curve. Chapman⁽³⁾ and others have attempted to improve the formula connecting viscosity with temperature, but these attempts always fail at low temperatures. Recently Hassé and Cook⁽⁴⁾ have considered a gas composed of Sutherland molecules, in which the attractive force varies as the inverse fifth power of the distance from the centre of the molecule. Their more exact formula gives a calculated force-constant which in certain cases may differ considerably from that calculated by means of Sutherland's formula, but the two formulæ give equally good agreement in the calculation of the coefficient of viscosity; the authors therefore conclude that the agreement of the experimental data with a theoretical relationship is by no means a safe check on the formula.

In a paper by Condon and Amringe⁽⁵⁾ a Maxwellian mean free path has been taken into consideration on classical lines, and some interesting remarks have been made upon Sutherland's constant, which in their viscosity formula would be about three-fourths of the ratio of the energy of two molecules at contact to the gas constant per molecule. Lennard Jones⁽⁶⁾ has put forward an interesting theory, but it is not proposed to discuss this in the present paper. There are also many empirical formulæ, such as that of Nernst, which fit the low temperature data over a limited range of temperatures; but no general formulæ connecting viscosity and temperature has yet been found, and the problem is not yet solved.

Another method of attacking this problem is by considering the possibility of unequal molecular complexity of the gas at different temperatures, and applying the laws of chemical dynamics to the equilibrium between the simple and complex molecules. Some years ago Dr. E. K. Rideal expressed to me the opinion that gaseous viscosities can be considered as a chemical phenomenon; Trautz⁽⁷⁾ and Duclaux⁽⁸⁾ have recently advanced the same idea. The phenomena of molecular association and dissociation can indeed be regarded as the simplest type of chemical reaction, a transition term to the formation of stable compounds.

Since the diameter of a molecule is increased by increasing its complexity, the coefficient of viscosity will be decreased.

At low temperatures, therefore, the experimental values should be below the theoretical values for non-associated molecules; but this is not the case, and the correction is still in the opposite sense to that required in order to make the experimental values fit Sutherland's curve. Thus my recent experiments on the vapours of organic substances⁽⁹⁾ always give high values for the viscosity-coefficient at low temperatures. If, however, we consider the viscosity values calculated by means of Meyer's formula of efflux, we see that the molecular weight enters the calculation as a vapour density, in such a way that an increase in its value leads to a higher calculated coefficient of viscosity. The value deduced for non-associated molecules must therefore be smaller than the real one whenever complex molecules are formed. The viscosity curve for a vapour undergoing association could then very nearly follow Sutherland's curve even at low temperatures, the normal increase of viscosity being compensated by the decrease due to larger molecular complexity.

In order to determine the real effect of molecular complexity on gaseous viscosity a series of experiments was made with acetic acid, since the anomalous behaviour of its vapour is well known, especially from the experiments of Ramsay and Young on its vapour densities. The acid (Schuchardt's acetic acid "puriss.") was purified by Orton and Bradfield's method⁽¹⁰⁾, with acetic anhydride in stoichiometric quantity and chromic oxide: the product was then fractionally crystallized out of contact from moisture, and fractionally distilled; the fraction boiling at 118.1° under 760 mm. pressure was collected. The final product melted at 16.6° C.

The viscosimeter was of the same type as described⁽⁹⁾ previously, with manometers on both sides of the capillary. It was quite suitable for this investigation, since it was possible to regulate the mean pressure and the temperature, and therefore to examine the substance at temperatures and pressures at which the substance is but little, if at all, associated. The dimensions of the capillary were

$$\sum \frac{l}{r^4} = 0.972 \times 10^9 \text{ cm.}^{-3}.$$

The evaporation thermostat was kept at about 50° C., whilst the condensation temperature was kept some degrees above zero so as to give a condensation pressure of about 6 mm. The densities have been taken from the data of Jaeger⁽¹¹⁾. The results of the experiments are collected in Table I. and

the mean values for a series of different temperatures are given in Table II.

The 93° values have not been corrected for slipping, in view of uncertainty as to the correct value of "R" to take, but they should not vary more than 2 or 3 per cent. The approximate value of the viscosity at that temperature can be taken as 0.78×10^4 C.G.S. at a mean pressure of 31 mm. The observations at higher temperatures have been corrected on the assumption that the vapour consists of simple molecules. Table I. leads to the conclusion that, especially at the higher temperatures, substantial changes in the mean

TABLE I.—Viscosity of Acetic Acid.

No.	Temp. in C°.	p_1 .	p_2 .	Δ .	Mass transpired gr. hour ⁻¹ .	$\eta \times 10^4$ C.G.S.	$\eta \times 10^4$ C.G.S. corr.
1...	93.7	5.925	0.63	34.70	0.115	0.769	
2...	93.7	5.93	0.63	34.83	0.114	0.783	
3...	92.1	5.03	0.65	24.87	0.083	0.775	
4...	150.5	6.07	0.72	36.33	0.080	1.140	1.168
5...	150.1	5.15	0.62	25.66	0.049	1.150	1.184
6...	200.2	5.16	0.62	26.24	0.039	1.304	1.350
7...	201.9	5.746	0.66	32.58	0.0492	1.309	1.351
8...	250.8	5.736	0.62	32.53	0.040	1.458	1.514
9...	248.2	5.746	0.63	32.62	0.047	1.441	1.494

TABLE II.—Viscosity of Acetic Acid. (Mean values.)

Temperature in C°.	η corr. $\times 10^4$ C. G. S.
93.2	0.770
150.3	1.176
201	1.350
249.5	1.504

pressures produce no marked discrepancies in the final values of the viscosity, so that the vapour must be supposed to obey the gas laws.

Another point to be observed is that the viscosities at the lowest temperatures differ considerably from those at the three higher points. The 150° point already shows a downward tendency which is opposite to that usually seen in vapours, and the 93° value is quite remarkably lower, so that a downward concave curve can be drawn between the experimental values. This is of interest because it seems to confirm the view that the upward concavity of the experimental curve for other vapours is not due to molecular

complexity, which sharply reverses the shape of the curve. We may with a good approximation obtain provisional values for Sutherland's constant from the data for the two highest temperatures until other data for still higher temperatures are available *. Sutherland's constant would then be $S=725$.

From a prolonged ideal line the viscosity at 0° has been extrapolated to $\eta_0=0.724 \times 10$, giving as the value of the mean collision area

$$\bar{A}=10.00\text{\AA}^2.$$

The mean area obtained seems to be of the right order of magnitude. Rankine found for methane a collision area of 7.7\AA^2 , and the dimensions of a COOH replacing an atom of hydrogen would be about 2.5 ångström square.

Using Meyer's formula to get the supposed molecular weight of the molecule at 93.7° from the extrapolated value of the viscosity, we get for the vapour density of the molecule 38.7 at a mean pressure of about 30 mm.: Ramsay and Young's value at 92° and at a pressure of 30.6 mm. is 39.8 . The agreement is fair, although the values now given are considered to be only approximate, since exact quantitative results can only be derived from experiments made over a larger range of temperatures and with greater exactness, and in comparison with observations on analogous compounds which do not undergo association. On the other hand, it is reasonable to suppose that the values now obtained for acetic acid between 150° and 250° represent the viscosity of the simple molecule.

Another datum about the coefficient of internal friction of acetic acid vapour exists in the literature, namely Meyer's and Schumann's value⁽¹²⁾. This would give at 119° a viscosity of 1.07×10^4 C.G.S., calculated on the basis of the theoretical vapour density, but, as the data are affected by an error of about 50 per cent., no useful purpose would be served by discussing them.

Summary.

1. The coefficient of internal friction of the vapour of acetic acid has been examined through a range of temperatures from 90° to 250° C.

2. The experiments have been made under reduced pressures, and the values from 150° to 250° are supposed to be those of the simple acetic acid molecule.

* Experiments are being set up for extending the range of temperatures to 500° .

3. The temperature-viscosity curve shows at lower temperatures an opposite shape to those of non-associated compounds.

4. The deviations from Sutherland's law are examined from different points of view and critically discussed.

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- (12) *Wied. Ann.* vii. p. 497 (1879).
- (13) See my note upon benzene. (*Proc. Roy. Soc.* 1929.)

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LXV. *The Viscosity of Vapours.*—Part II. *Relationships between Critical Constants and Gaseous Viscosity.* By A. G. NASINI, *Ph.D.**

FROM a consideration of the properties of systems which are mechanically and statistically similar, Kamerlingh Onnes⁽¹⁾ has deduced some relationships between the viscosity of liquids and the critical constants. Similar relationships ought to exist also for gases. Thus, from the simple kinetic formula for the viscosity of gases

$$\eta = \frac{1}{3} mn \bar{c} l$$

(where η is the viscosity, m is the mass of the molecule in grams, n the molecules per c.c., l the mean free path, and \bar{c} the mean molecular velocity) we get by the substitution of suitable functions of the molecular radius, temperature, and critical density the following formula :

$$C = T^{\frac{1}{2}} m^{-\frac{1}{2}} \rho_c^{\frac{2}{3}},$$

where $C = \frac{1}{3} \frac{0.7071}{\pi} \sqrt{3R} 2\pi^{\frac{2}{3}}.$

* Communicated by Prof. T. Martin Lowry, F.R.S.

In this formula, T is the absolute temperature, ρ_c the critical density, and R the gas constant. Writing $M = mn \times 22414$, we obtain for the viscosity η_c at the critical temperature the relationship

$$\frac{\eta_c m^{\frac{1}{2}}}{T_c^{\frac{1}{2}} \rho_c^{\frac{2}{3}}} = C, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T_c is the critical temperature in K° and M is the molecular weight. In a similar way the equation

$$\eta_c \sqrt[6]{\frac{T_c}{M^3 \rho_c^4}} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

may be obtained, which is Kamerlingh Onnes's relationship for liquids, where p_c is the critical pressure. Instead of the ratio M to ρ_c , we may insert the critical molecular volume.

In Table I. are collected the values necessary for calculations, together with those of the constant obtained from formulæ (1) and (2).

The viscosities used for the calculations are the most probable values selected from Landolt and Börnstein's Tables (1923 edition). The extrapolation and interpolation of the data for moderate and high temperatures have been made by Sutherland's formula, finding the constants where they had not been worked out previously.

The value of η_c for helium has been extrapolated from Günther's (2) values by means of Nernst's empirical formula. The exponent of the formula has been taken as unity, which is the maximum mean value found; this value is obviously rather uncertain, since experiments to show the behaviour of the viscosity curve $5^\circ K$ have not yet been made. If Nernst's formula were right, the value of the exponent ought to reach 1.5. The data for hydrogen, which were interpolated by means of the same formula, are more certain, although it was not expected that the constants would be very accurate at low temperature, where the imperfection of the gas would be very obvious.

For benzene and acetic acid I have taken my own values, for ammonia and carbon dioxide the last values of Edwards & Worsick and of Smith⁽³⁾.

The table shows that the agreement is quite good for the substances considered, and, indeed, the mean error of the calculated constants (6-7 per cent.) corresponds closely with the mean error of the experimental data. It is interesting to note that the constant of equation (1) gives divergent values for bromine, whilst it gives good values for water and acetic

acid, substances which usually show discrepancies in formulæ based upon the theory of corresponding states. The values calculated by equation (2), however, show an abnormal behaviour for the last two named substances, whilst chlorine also diverges from the mean values.

Taking 2.80×10^{-5} as the mean value for constant (1), the critical density of krypton ought to be 0.873; the value given by Goldhammer⁽⁴⁾ is between 0.694 and 0.927.

TABLE I.

Substance.	M. weight.	Critical density.	η at critical temperature $\times 10^4$ C.G.S.	Critical temperature.	Critical pressure atm.	$\frac{\eta_c M^{1/3}}{\rho_c^{1/2} T_c^{1/2}} \times 10^5$.	$\frac{T_c}{M^{3/2} \eta_c} \times 10^6$.
Helium	4	0.065	0.086	5	2.3	3.01	3.23
Hydrogen	2	0.033	0.155	33	13	2.95	3.55
Nitrogen	28	0.311	0.867	126	33	2.93	3.54
Carbon monoxide ...	28	0.311	0.934	134	35	3.06	3.73
Argon	39.9	0.531	1.253	151	48	2.87	3.47
Oxygen	32	0.43	1.166	155	49.5	2.93	3.53
Methane	16	0.162	0.750	190	45.6	2.90	3.52
Ethylene	28	0.21	0.950	283	50.6	2.80	3.36
Xenon	130.2	1.15	2.266	288	58	2.74	3.40
Carbon dioxide	44	0.46	1.521	304	72.8	2.75	3.41
Ammonia	17	0.236	1.405	405	112	2.93	4.00
Chlorine	79.9	0.573	1.897	417	76	2.74	5.00
Isopentane	72.1	0.234	1.111	463	33	2.77	3.54
Ethyl acetate	88	0.307	1.384	523	38	2.81	3.70
Benzene	78	0.304	1.42	561	48	2.74	3.59
Bromine	159.8	1.18	2.874	575	—	2.50	—
Acetic acid	60.04	0.35	1.65	594	58.1	2.70	4.12
Water	18	0.329	2.315	647	217	3.09	4.44

The critical viscosity of neon by extrapolation to the critical temperature would be 0.691×10^{-4} .

Several empirical rules connecting viscosity at the critical temperature with other constants have been found by Rankine. One of the rules is

$$\frac{\eta_c^2}{A} = \text{const.}, \quad (3)$$

where A is the atomic weight, valid for the rare gases and the halogens. The constant is not universal, but differs for

the two groups of the periodic system. If this relation were true for molecules, equation (1) would become

$$\frac{\eta_c^2}{M} = \frac{T_c \rho_c^{4/3}}{M^{4/3}} C^2 = \text{const.},$$

where C is the constant of equation (1). Since the molecular critical volume, v_c , is equal to M/ρ_c , the constant of equation (3) will have equal values when the ratio $\frac{T_c}{v_c^{4/3}}$ is also equal.

The molecular critical volume and temperature vary for the halogens and the rare gases with a certain regularity with increasing molecular weight; the gaseous viscosity at the critical temperature, which is connected intimately to these two quantities, may therefore be expected to show the same regularities.

Some values of $\frac{\eta_c^2}{M}$ are tabulated in Table II., where chlorine and bromine are seen to give similar values for this ratio.

TABLE II.—Viscosity at the Critical Point.

Substance.	$\frac{\eta_c^2}{M} 10^{-10}$.	Substance.	$\frac{\eta_c^2}{M}$.
Helium	0.185	Ethylene	3.22
Hydrogen	1.2	Xenon*	3.93
Nitrogen	2.68	Carbon dioxide.....	5.25
Carbon monoxide...	3.14	Ammonia	11.6
Argon *.....	3.93	Water.....	29.8
Oxygen	4.25	Chlorine	5.07
Methane	3.52	Bromine.....	5.17

* Rankine's values.

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- (4) See J. W. Mellor's 'A Comprehensive Treatise of Inorganic and Theoretical Chemistry,' vii. p. 918 (1927).
- (5) A. O. Rankine, Proc. Roy. Soc. lxxxiv. A, p. 190 (1910) and other papers.

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LXVI. *On the Origin of the Electrodeless Discharge.*By K. A. MACKINNON, *M.Sc.**

1. **A**LTHOUGH the electrodeless discharge was discovered as long ago as 1884, there are still conflicting views regarding its origin. Experimental evidence has been given by many writers (Lehrmann ¹, Tesla ², Lecher ³, Steiner ⁴, etc.) that the discharge is the result of the large alternating potential differences which exist between the ends of a coil carrying high-frequency currents, while according to Hittorf ⁵, its discoverer, and to J. J. Thomson ⁶ the discharge is due to electromagnetic induction. As recently as 1927, Thomson ⁷, using excitation by spark discharges, has given additional experimental evidence supporting the view which he has always held. This paper was followed by one by Townsend and Donaldson ⁸ criticizing the electromagnetic view. They point out that theoretically the electrostatic intensity (E_s) between the ends of a solenoidal coil of ordinary dimensions is more than thirty times the electromagnetic intensity (E_m) around a ring inside the coil. Thus they are led to conclude that the electrostatic forces are largely responsible for the electrodeless discharge. In support of this conclusion they give experimental evidence obtained with the use of continuous wave (c.w.) excitation.

In view of the apparent conflict between these two recent articles, the work of the present paper was undertaken.

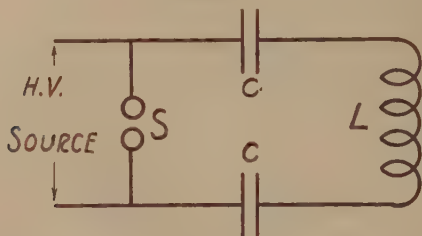
2. At the outset it may be stated that Thomson's work has always been confined to the *ring* type of discharge which appears within a small range of pressures, while Townsend and Donaldson were dealing with a glow discharge obtainable over a much wider range. The work herein described indicates that the ring discharge is undoubtedly of electromagnetic origin, whilst the glow is largely or entirely electrostatic. In one sense, therefore, both are right. The failure of Townsend and Donaldson to recognize the difference between the two types of discharge seems to be the cause of the discrepancy.

* Communicated by Prof. J. K. Robertson. The writer undertook this work while a holder of a Bursary granted by the National Research Council of Canada, Ottawa.

Experiments with Damped Oscillations.

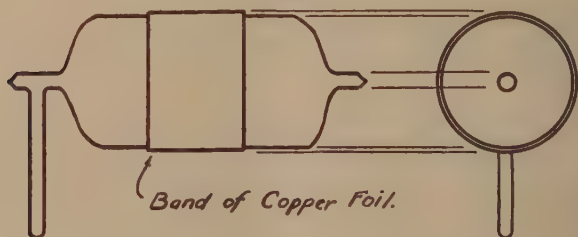
3. In this investigation, observations were made with both spark and c.w. excitation. The usual spark excitation circuit (fig. 1) was employed. S is a micrometer gap, C Leyden-jars, and L a coil of a number of turns of heavy wire which fit around the cylindrical discharge bulb. The

Fig. 1.



discharge bulbs used were 16 cm. long and 11 cm. in diameter (fig. 2, ignore copper band). The vapour in the bulb was either iodine or mercury. These substances were selected owing to the fact that each of them, on being subjected to a gradually increasing excitation, will change suddenly the colour of its discharge. Iodine breaks into

Fig. 2.



an intense green from a yellowish colour, whilst mercury jumps from a dull white into a dazzling white discharge. It is assumed that when this transition occurs, the forces acting on the exciting electrons have a definite value. These changes are obtained only if the pressure of the vapour be within a certain interval. In iodine the pressure was regulated by keeping the projecting stem of the bulb at a fixed temperature, generally 0°C . In the

case of mercury, as temperatures of between 50° and 100° C. were necessary, observations were made with the bulb in an electrically heated oven.

4. As the gap is gradually increased, many changes take place in the appearance of the discharge in iodine at 0° C. For very low excitations, there is a faint yellowish glow which extends from end to end of the bulb. This glow is weaker near the axis of the coil, but stronger in the central plane. As the excitation increases, the glow becomes brighter and brighter around the central plane, and finally breaks into a fitful green ring in that plane. This central ring is so bright that the glow formerly extending throughout the bulb is not noticeable. For still greater gaps several more green rings form near the central plane, until finally all these rings merge into one broad green annular band which extends nearly the length of the solenoid. The radial thickness, however, remains the same.

5. To ascertain the origin of the different types of discharges described above, the following experiments were performed :—

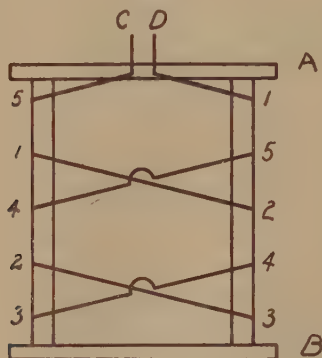
(a) The discharge bulb was held next to, but outside, the exciting coil. In this position the electrostatic forces have the same opportunity for ionizing as is the case when the bulb is inside the coil, but the electromagnetic forces are absent. The gap was adjusted so that, with the bulb inside the coil, the green ring was readily obtained. Then the bulb was placed outside, but next to, the coil. The discharge was merely a faint glow similar to that obtained with low excitation on the bulb inside the coil. This experiment demonstrates that, although the E_s between the ends of the exciting coil be high, the resulting electrostatic discharge is a relatively faint effect.

(b) In order to investigate the green ring discharge a loop of thin copper foil about 3 inches wide, closed on itself, was made to fit snugly over the discharge bulb (as in fig. 2). The gap was adjusted so that the iodine bulb (without the foil) gave a solid green annular band extending up and down the bulb. Then the bulb was removed from the coil, the foil slipped over it, and the bulb replaced. It was found that all green effects were absent inside the foil, but still remained at the exposed ends

of the bulb. Also the faint yellowish glow obtained by holding the bulb against the outside of the coil (as in 5(a)) was obtained equally well with the copper foil in place. From this experiment it is concluded that the green ring is of electromagnetic origin.

(c) The effect of a peculiarly wound solenoid (fig. 3) similar to that used by Townsend and Donaldson⁽⁸⁾ (coil G_2) was investigated. With this method of winding, the electrostatic field between the two ends is practically nil, but the electromagnetic field is about the same as in the case with an ordinary solenoid. Townsend and Donaldson found that, using this type of coil, the discharge obtained

Fig. 3.

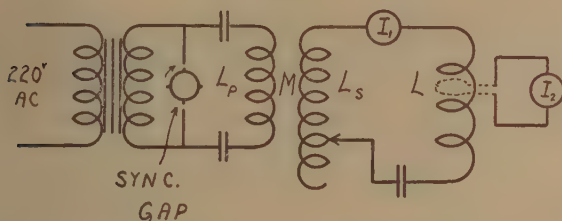


with c.w. started between the open ends CD, thus demonstrating the electrostatic origin of that discharge. With a solenoid of this kind, and spark excitation, observations were made by the writer with iodine. It was found that, for short gaps, there was a faint glow outlining the wires near the open end A of the coil, but no discharge at all at the closed end B. As the gap was increased, this glow also increased in intensity. As a certain gap length was reached however, there appeared *in the central plane of the coil* a yellowish ring, which suddenly broke into the ordinary green ring with any further increase in gap-length. The fact that the green ring occurred only at or near the central plane of the coil indicates that the ring is of electromagnetic origin.

(d) In order to make sure that the above results were not peculiar to iodine, the above experiments were repeated with mercury vapour, with similar results.

(e) In a spiral coil the electrostatic forces act radially outward from the inner turns so that the effect in an electrodeless bulb placed inside such a coil must be solely of electromagnetic origin. In the following experiment a spiral coil was made of such dimensions that it produced the same E_{eff} in the bulb as the ordinary solenoid, when the frequency and the value of the currents through the coils were the same. To find the required dimensions of the spiral, a loop of wire of the same diameter as the inside surface of the discharge bulb (the green ring has this diameter) was shorted through a hot-wire ammeter (I_2 in fig. 4). This was placed in the central plane of the

Fig. 4.



solenoid L . The coil L was in a tuned secondary circuit coupled to a fixed primary circuit excited by a synchronous rotary gap. The ratio of loop current (I_2) to secondary current (I_1) was determined for various values of current. Following this, solenoid L was replaced by the spiral, and the loop placed in its plane. The turns on the spiral were then adjusted to give the same ratio of I_1 to I_2 . In the following test this length of spiral and this frequency were always used.

Observations were made of the gap-length just necessary to give the green ring during a flash, using the solenoid and then the spiral. The high voltage was applied to the gap only in short flashes with an interval of longer duration between the flashes. As the inductance of the spiral was greater than that of the solenoid, it was necessary to retune the circuit to the fixed frequency used whenever the coils were interchanged. This was done by varying either the

capacity of the oscillating circuit or the value of a separate tuning inductance. The results were slightly different, depending on which of these was altered during the retuning. In order to get steady conditions, an air-blast across the gap was used throughout. The values of the current given are for continuous discharge. The following results were obtained :—

	Spiral.	Solenoid.	Solenoid.
Wave-length.....	275 m.	275	275
Tuning inductance	1 turn.	1	4
Capacity	2 jars.	3	2
Current	4.6 amp.	5.2	4.5
Gap-length	8.5 mm.	6.3	8.5

If the electrostatic forces actually have an effect in forming the ring discharge, one would expect that the gap for the solenoid would be very much less than that for the spiral. Yet an examination of the results given in the above table indicates that *the critical gaps are of the same order of magnitude in the two cases*. Although, in the writer's opinion, little reliance can be placed in spark-gap readings for exact measurements, yet their accuracy here should be sufficient to demonstrate that the ring discharge is undoubtedly of electromagnetic origin.

The conclusions to be drawn from the above experiments are that with low excitations the discharge is electrostatic, but with higher excitations, when the bright ring appears, the discharge is of electromagnetic origin. Also, discharges of electrostatic origin are always of low luminosity, even though the electrostatic intensity be very high.

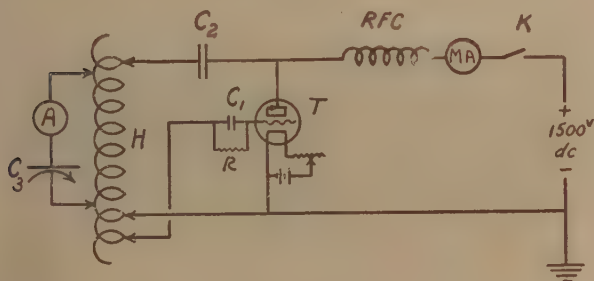
Experiments with Undamped Oscillations.

6. As Townsend and Donaldson had worked with c.w. only, the above experiments were repeated with this mode of excitation.

The generator used was a Hartley circuit as shown in fig. 5, involving a vacuum-tube oscillator of 250-watt rating fed by a 1500-volt d.c. generator. The discharge bulb was either inserted in the Hartley helix H. or in a coil connected in a tuned circuit magnetically coupled to H.

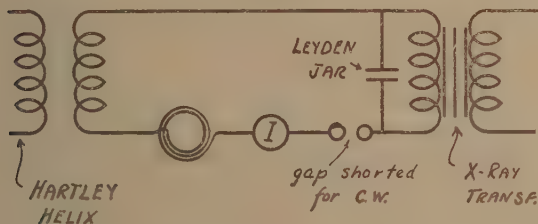
(a) The result, at first surprising, was that with the iodine bulb in coil H no green ring or ring of any kind could be obtained with undamped excitation. For certain adjustments the high-frequency current through th

Fig. 5.



helix was more than 6 amperes, and yet with spark excitation the green ring appeared for currents of less than 3 amperes. The discharge actually obtained with c.w. was a solid glow throughout the bulb. The appearance was the same whether the bulb was held inside or outside next the coil. Also, the presence of the copper-foil loop around the bulb had no effect on this solid glow. These facts indicated that the discharge with c.w. excitation in iodine was of electrostatic origin.

Fig. 6.

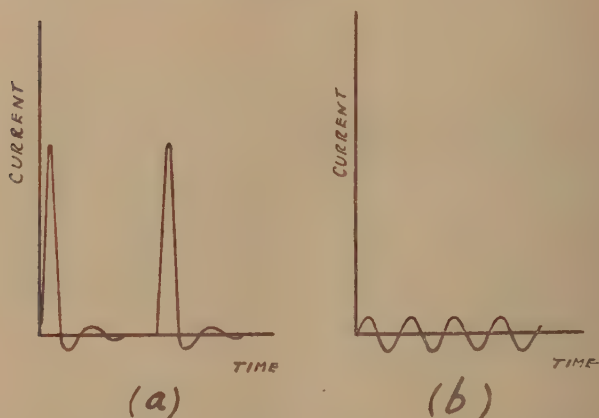


To eliminate the possibility that the difference in the capacities of the exciting circuits (air dielectric for c.w., glass for spark) might account for the failure to get the same discharge, the circuit of fig. 6 was tried. A pancake coil was used, as electromagnetic effects are more readily detected with it. It is seen that the identical exciting

circuit was used for both damped and undamped methods. The circuit was tuned to a wave-length of 171 metres. It was found that with a current of 5.5 amps. no discharge at all was obtained with c.w., but the spark gave a green ring with a current of 4.6 amps.

The probable explanation of the failure to obtain a ring discharge with c.w. is found in the difference between the graphs of "current *v.* time" for the two cases, (fig. 7 (*a*) spark, (*b*) c.w.). From these it is evident that, although the root-mean-square values (as indicated on hot-wire meters) of the currents in the two cases may be the same, the maximum value of the current during the first half-cycle of the spark current is enormously greater than that of

Fig. 7.



the c.w. current. As the maximum velocity acquired by an electron depends on the magnitude of the field intensity during the half-cycle, it follows that the excitation will be very much more intense in the spark case.

(*b*) From this explanation it is seen that, if the vapour were easily enough ionized, a ring discharge should occur even with c.w. excitation, and experiments with mercury vapour seemed to indicate the truth of this. With a constant current of about 6 amperes the discharge in mercury was examined as the bulb was gradually heated. At lower temperatures the glow was a dull white. After a temperature of 50°C. was attained a very bright white discharge filled the whole bulb and the solenoid current

dropped to 2 amperes, indicating the presence of heavy currents in the gas. As the temperature still rose the central part of the bulb became darker and darker, and finally at 140°C . the bright white discharge had dwindled to a bright white ring in the central plane of the solenoid—that is, it had the same appearance as the white ring obtained with spark. This ring disappeared suddenly at about 165°C ., leaving an emerald-green glow filling the whole bulb. On cooling, the ring commenced again. It was found that the value of the wave-length had little effect on the change to the bright white discharge, but the capacity of the exciting circuit had to be kept low. For instance, if the air condensers were replaced by a leyden-jar, no bright white discharge could be obtained. But on replacing this jar by two tiny jars (1 in. diam., 3 in. high) in series the white discharge was readily obtained.

Using the three tests of 5 (a), (b), (c), it was readily shown that this bright white discharge in mercury was of electromagnetic origin, and also that the dull white discharge obtained with low excitations was of electrostatic origin.

Discussion.

7. It will be noticed that for low excitations the discharge was electrostatic, but as the excitation increased the electromagnetic discharge commenced suddenly, and was of much greater intensity than the previous electrostatic discharge. Now, Townsend and Donaldson showed (and experiments by the writer have confirmed their observations) that the ratio of E_s to E_m is greater than thirty for an ordinary solenoid. In the case of the solenoid of fig. 3, E between C and D is obviously very much greater than thirty times E_m around the inner surface of the bulb. On the other hand, the experiments presented in this paper indicate that, although *outside* the bulb E_s is so much greater than E_m , *inside* the bulb E_s must be either much less than E_m , or the exciting electrons in the electrostatic path cannot, for some reason, acquire as high a velocity as those in the electromagnetic path.

As regards the first suggestion, it was always noticed that when the electrostatic glow was taking place in any of the bulbs, the glass walls in the path of the electrostatic field got very hot quickly. This indicated great dielectric losses in the glass at the high frequencies used. The only

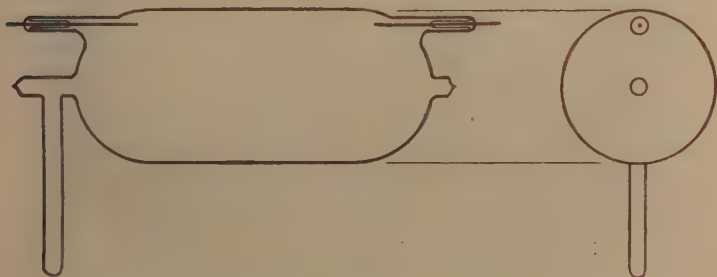
difference between the path of the electrostatic field and that of the electromagnetic field is that the former traverses two layers of glass before the gas is reached, while the path of the latter is entirely within the gas. The fact of the high dielectric losses in the glass suggests that the glass is acting appreciably as a very high resistance in the part of the electrostatic field which it occupies. For certain low excitations the value of E_e is almost negligible, but that of E_s , since it is over thirty times greater than E_e , must be sufficient, after subtracting the potential drop through the glass walls, to cause weak ionization in the gas. This gives rise to the faint electrostatic glow one gets with low excitations. As the excitation is increased, the current tends to increase through the electrostatic path (glass to gas to glass). An increase in current through the gas means an increase in ionization of the gas, and thus a lowering of its effective resistance to the electrostatic voltage. Hence, although the total electrostatic voltage across the circuit is higher, the proportion of the voltage used up in the gas is less, because the resistance of it has dropped whilst the resistance of the glass has remained the same. Thus, even though E_e increases externally, it does not do so at the same rate internally. On the other hand, E_m increases directly with the excitation. When ionization starts in the ring path, the resistance drops, but since the whole electromagnetic E.M.F. is always applied to the ring circuit, the current in the path must increase more quickly than E_m . Thus intense ionization sets in around the ring when E_m attains a certain value.

With reference to the second suggestion, it is noticed that the electrons moving in the electromagnetic field meet no obstruction, but those in the electrostatic field have a glass wall to strike at either end of the path. Any electrons striking the wall are lost so far as ionizing is concerned. Hence, if, for the pressure at which the electromagnetic ring discharge takes place most readily, the mean free path of the electrons be about equal to the distance between the glass walls in the electrostatic path, then no electrostatic discharge could be expected, even though E_e be greater than E_m inside the bulb.

8. In order to investigate the above possibilities experimentally, a tube fitted with tungsten electrodes, as illustrated in fig. 8, was used. At first it was filled with

iodine vapour in the ordinary way, but it was found that no ring discharge could be obtained, thus rendering the bulb useless for comparison with the bulbs without electrodes. It is possible that the presence of the tungsten electrodes prevented the formation of the ring, an effect

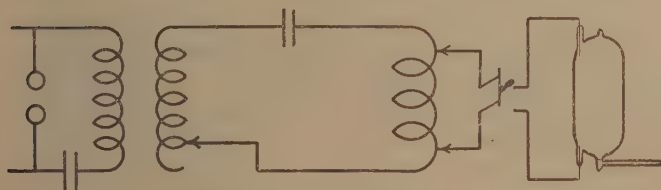
Fig. 8.



observed by Thomson⁽⁷⁾ for certain impurities. It was thus necessary to use a continuous flow of gas through the bulb by connecting one tip of the bulb to a pump and letting the gas leak slowly into the other end of the bulb.

The gases tried were nitrogen, oxygen, and air, for all of which the general results were the same. The exciting circuit was arranged as in fig. 9 for the electrostatic effect, or with the bulb inside the solenoid in the ordinary manner

Fig. 9.



to get the electromagnetic effect. With the bulb inside the solenoid, and at the same time with the electrodes connected to the ends of the solenoid, the general effect in all three gases was the same. For instance, with nitrogen, from a high pressure of about 1.163 mm. down to about 0.0062 mm. there was no ring discharge, but there was a bright line discharge between the electrodes. At the pressure 0.0062 mm. this discharge ceased and the ring

discharge commenced. Around this pressure both discharges took place simultaneously. At 0.00017 mm. the ring discharge ceased and there was no discharge at all in the bulb.

These facts indicate that here the mean free path (pressure) is the predominating factor. For short free paths the high E_s between the electrodes causes intense ionization, but the E_m is too small to cause any ring discharge, as the electrons have collisions before acquiring enough velocity. When the pressure is so low that the mean free path is comparable to the distance between the electrodes, then the discharge between the electrodes ceases. But the electrons in the electromagnetic ring path have a sufficiently long free path to acquire enough velocity to cause ionization, thus causing the ring. It is at this low pressure that the iodine and mercury bulbs were used, because these bulbs were worked at a temperature which passed the electromagnetic ring discharge most readily. On the other hand, it should be noticed that at the high pressures where the *electrode* discharge passed readily there was no discharge whatever when the electrodes were disconnected from the ends of the exciting solenoid. Thus the electrostatic drop across the coil in the latter case must be reduced by the glass, as suggested previously. This explanation involving the mean free path fails to account for the weak electrostatic glow obtained in both iodine and mercury before the ring discharge commences.

The writer wishes to acknowledge his indebtedness to Prof. J. K. Robertson, at whose suggestion this work was undertaken, for his advice and criticism, and to Prof. D. M. Jemmett for the loan of apparatus and for suggestions regarding the work.

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Kingston, Canada, July 1929.

LXVII. *On the Study of the Spectrum of Oxygen under Different Conditions of Excitation.* By D. B. DEODHAR, M.Sc., Ph.D., Reader in Physics, and S. K. DUTT, M.Sc., Lucknow University, Lucknow, India*.

[Plate XII.]

RECENTLY a good deal of attention has been directed towards the investigation of the line as well as the band spectrum of oxygen. The important investigations on the atomic spectrum are by A. Fowler†, McLennan and others‡, and Hopfield§. Among the workers on the molecular spectrum are Holland||, Frerichs¶, and Ellsworth and Hopfield**. Holland has observed a few groups of bands in the visible. Frerichs has measured the Q branches of five negative bands in the visible, namely, $\lambda\lambda$ 6856, 6419, 6026, 5632, and 5295. Ellsworth and Hopfield have made measurements of some bands of oxygen in the ultra-violet. Lockrow†† has mainly investigated the critical potentials of oxygen. Recently Johnson‡‡ has measured the band lines of a group of bands in the ultra-violet.

However, it appears that even now the work of classification and measurement of lines and bands due to oxygen is not complete and that further experimental work is desirable in order to throw more light on the problem. It was with this view that we began the experimental study of the behaviour of the spectrum of oxygen under two different conditions of excitation, and the object of the present communication is to put forth the preliminary account of some interesting observations on a typical type of discharge compared to the usual Geissler tube discharge in oxygen.

* Communicated by the Authors.

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‡ McLennan, McLeod, and McQuarrie, Proc. Roy. Soc. vol. cxiv. pp. 1-22 (1927).

§ J. J. Hopfield, Astrophys. Journ. vol. lix. pp. 114-124 (1924).

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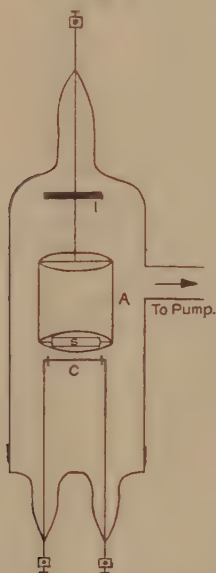
†† L. L. Lockrow, Astrophys. Journ. vol. lxiii. pp. 205-217 (1926).

‡‡ R. C. Johnson, Proc. Roy. Soc. vol. cv. pp. 683-691 (1924).

Experimental Procedure and Observational Data.

The special discharge-tube (fig. 1). was made of transparent quartz made by the Thermal Syndicate Company of England. The anode A was made of thin nickel sheet rolled into the form of a cylinder. The length and diameter of this hollow cylinder were approximately 5 cm. and 2.5 cm. respectively. The bottom of the cylinder was closed with a plane nickel sheet. A small

Fig 1.



rectangular slit S about 2 mm. wide and 10 mm. long was cut in the central portion of the bottom of the cylinder; and a long vertical slit about 3 mm. in width was cut into the side of the cylinder. This cylindrical anode, to which a small piece of iron I was attached, was mounted on a long brass screw, and the anode could be moved backwards and forwards by means of a suitable electromagnet working from outside the discharge-tube. Such an arrangement was very useful in adjusting the distance between the filament and the anode without disturbing the discharge-tube. The cathode C was made of a thin

platinum strip 10 mm. long and 1.5 mm. wide. The middle portion of this strip was coated with barium oxide, and this oxide-coated filament when heated by an electric current served as a strong source of electrons. The filament was adjusted in such a way that it was parallel to the bottom slit of the nickel anode. The nickel chamber could be charged to a positive potential of any value lying between 2 volts and 150 volts by means of a slide-wire potentiometer arrangement. The stream of electrons shooting from the middle portion of the filament passed through the bottom of the anode into the anode chamber and collided with the gas molecules there. The luminous stream resulting from such a collision of electrons and gas molecules could be viewed through the window cut on the side of the cylindrical anode as mentioned above. As the anode is charged to a certain definite potential, the internal volume being enclosed by an equipotential surface is "field free," and such a kind of discharge may be conveniently called a "field free discharge."

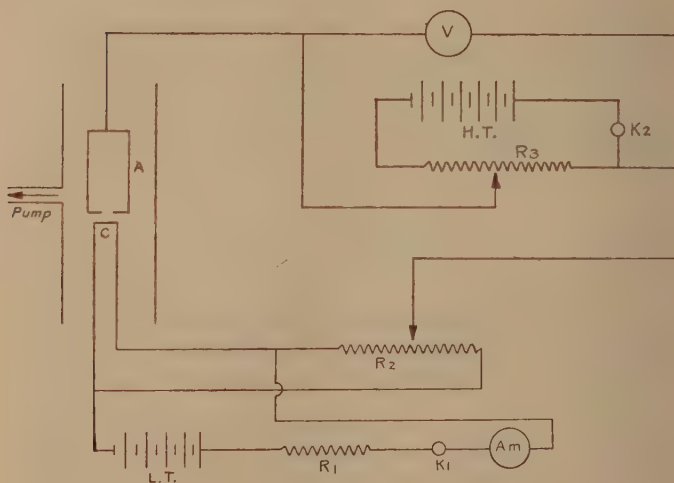
Preparing the Oxycoated Filament.

After a number of trials we found a very effective method of coating the filament; and we should like to make a note of the procedure here, in view of the fact that the oxide usually rather falls off quickly from a coated filament. A small quantity of highly pure barium nitrate should be taken and its saturated solution should be made in distilled water in a test-tube which is first carefully cleaned and rinsed with boiling distilled water. A glass rod with a pointed end should be also well cleaned and rinsed in boiling distilled water just before use and put into the test-tube containing the saturated solution of the nitrate. The platinum filament should be electrically heated to redness before treatment and then the current should be switched off. A drop or two of the solution should then be put on the central portion of the filament with the help of the glass rod and the filament should be held above an extremely low bunsen flame to allow the drop to dry slowly. After the drop is dried up another drop of the liquid should be placed on the previously dried drop and the slow drying repeated. In this way a fair amount should be deposited at the required spot. After this the filament should be again electrically heated

to redness so that the nitrate melts and changes into oxide. The current should be kept on for a few seconds and then it should be gradually reduced to zero. In this way a very hard coating of barium oxide is formed on the filament. The process of putting more drops and drying and electrically heating may be repeated twice or thrice to get a good deposit. The deposit of oxide so obtained sticks very fast and its life is found to be 100 hours of actual use.

The discharge-tube with its anode and filament is shown in fig. 1, while the electrical circuit is shown in fig. 2. The

Fig. 2.



heating-current for the filament was taken from a low-tension battery of accumulators L.T. with an adjustable resistance R_1 . The main source of the electrons was the central part of the filament, and in order to measure the voltage between the anode and the centre of the filament the following device was used. A large slide-wire resistance R_2 of 1300 ohms was placed in parallel with the filament, and the negative terminal of the high-tension battery H.T. was connected to the middle point of this resistance. The potential of the middle point of the filament is practically the same as the middle point of the high resistance, and so it could be safely accepted that the

applied voltage was between the anode and the middle point of the filament. The voltage was measured by the voltmeter V as shown in the figure. The filament could be taken out and sealed in at will.

The Vacuum System.

The vacuum system was composed of all glass joints except for the quartz discharge-tube, which was joined to the system by a sealing-wax joint. The rough vacuum was prepared by the Cenco Hyvac pump and the fine vacuum was obtained by Gaede's single stage diffusion pump backed by the Cenco pump. CaCl_2 and P_2O_5 were used in order to absorb water vapour, and NaOH was used as an absorbent of carbon as CO_2 . The pressure was measured by a MacLeod gauge. With this arrangement a vacuum of the order of 10^{-4} mm. of mercury could be easily obtained. A Geissler tube was also attached to the side of the vacuum system so that its discharge could be viewed in the end-on position. The source of oxygen was a quantity of highly pure potassium permanganate crystals stored in a glass tube which was sealed to a spherical glass reservoir of about 150 c.c. capacity. This reservoir also formed a part of the vacuum system. The oxygen from the reservoir could be supplied to the system or shut off from it by means of a tap. Before entering the discharge-tube the oxygen had to pass over the drying agents and NaOH. Finally, the discharge-tube could be shut off from the system by means of taps.

After the whole of the apparatus was set up as described above, the Hyvac pump was started and when, with all the stopcocks open, the MacLeod gauge registered a pressure of about one-tenth of a millimetre, the diffusion pump was also started, and in about half an hour's time the pressure indicated by the gauge was 10^{-3} mm. The pumps were kept on and the glass tubes were baked as far as possible by means of a bunsen flame playing on them to take off the occluded gases. The permanganate was afterwards heated carefully. The oxygen thus given out was passed through the whole system and was pumped out. Several such washes of oxygen were given, and the observations were attempted when it was found that there was no detectable leakage eighteen hours after the pump was disconnected.

It was found by trials that at a pressure of about 0.2 to 0.3 mm. the spectrum of oxygen seen through the pocket spectroscope was fairly intense and that it contained a large number of lines and bands. The glow of the discharge of the Geissler tube was greenish yellow at this pressure. The Geissler tube was excited by an induction coil worked by a four-volt battery.

The colour and other spectral peculiarities in the low-voltage tube were dependent on the anode voltage and the pressure. The filament was kept at a distance of about one millimetre from the anode. For the same pressure the colour of the glow in the tube was yellowish, green, and pink at 30, 40, and 50 volts respectively. The change in colour is associated with a change in the spectrum, and thus we could obtain varieties of spectra observed for the same gas at different exciting voltages.

Our main object has been to look into the band spectrum of oxygen, and as at 50 volts the spectrum showed a number of band groups we restricted our observations to the discharge at 50 volts. The heating-current in the filament was kept at 4.5 amps. In the beginning of the work the green mercury line used to come up as an impurity, but repeated washes of oxygen made it very faint, and at a pressure of 0.2 to 0.3 mm. it was completely suppressed. It was curious that the hydrogen lines H_{α} and H_{β} appeared persistently in the discharge-tube and they could not be suppressed. When the visual observations through the pocket spectroscope showed that the character of the spectrum was the same for the same conditions of excitation and pressure, it was decided to photograph the spectra by means of a Hilger's constant deviation spectrograph. The Geissler tube was arranged in the end-on position, and its glow was focussed upon the slit of the spectrograph by means of a cylindrical lens. The exposure time was three and a half hours. In order to photograph the "field free" discharge the slit of the spectroscope was directed to the stream of light which appeared inside the cylindrical anode and an exposure of three and a half hours was given in this case also. An iron arc comparison spectrum was taken between the two spectrograms. Several plates were taken in this manner, and it was found that each plate showed a remarkable difference between the two spectra. Some lines and bands which were prominent in intensity in the Geissler tube appeared as weak in the "field free"

discharge and vice versa ; and some lines which were not present in the one came out quite strong in the other. The accompanying plate (Pl. XII.) shows this behaviour in a striking manner. The low dispersion of the spectroscope could not allow the accurate measurement of the lines on the plate ; but there was not much difficulty in identifying the prominent lines and bands with the help of the important iron arc lines on the plate and with the help of the oxygen lines given in the atlas prepared by Eder and Valenta. Certain lines were identified with the help of the list of wave-lengths given in Kayser's 'Handbook of Spectroscopy,' vol. vi. Some of the important observations from the plate are given below. For a quick reference the lines on the plate are numbered. The lines of the low-voltage discharge are given in dashed numbers to distinguish them from the Geissler tube lines.

Observations.

- 1 & 1' represent the hydrogen line H_{α} .
- 2 & 2' represent the oxygen line 6460, which is stronger in the low-voltage discharge than in the Geissler tube.
- 3 denotes a line 6276 which is absent in the low-voltage discharge.
- 3' is a band head near λ 6430 which is absent in the Geissler tube.
- 4 is the oxygen line 6171 and it is fainter than 4'.
- 5 is a band head λ 6032 and it is much stronger than 5'.
- 6 is another band head λ 5630 which comes out stronger than 6'.
- 7 is a band head λ 5290 and it is also stronger than 7'.
- 8, 9, & 10 are lines 5130, 5020, & 4924, and these are not present in the low-voltage discharge.
- 11 & 8' represent H_{β} .
- 12 is a band head λ 4830 which is much stronger than what comes out in 9'.
- 13 & 14 are oxygen lines 4710 & 4706 which are absent in the low-voltage discharge.
- 15 & 10' denote the line 4699, where 10' is very strong compared to 15.
- 16 & 11' denote the line 4639, where 11' is stronger than 16.

- 12' & 13' are lines 4609 and 4596. Both of these are absent in the Geissler tube.
- 17 & 14' represent the line 4591, where 17 is stronger than 14'.
- 18 & 15' denote the line 4540, 18 being stronger than 15'.
- 19 is $\lambda 4516$, which is absent in the low-voltage discharge.
- 20 represents a strong band head whose value is about $\lambda 4500$, and corresponding to this there is 16', which is a faint indication of the same.
- 21 & 17' represent the line 4417, and both of them are nearly equal in intensity.
- 22 is the line 4396 fainter than 18'.
- 23 & 24 is a pair of lines 4367 and 4352 which is better defined than 19' and 20'.
- 25 is the line 4337, which is much weaker than 21'.
- 22' & 23' are lines $\lambda\lambda 4320$ and 4303, and both of them are absent in the Geissler tube discharge.
- 24' is the line 4275, which is much stronger than 26.
- 27 & 25' denote a faint band head 4260, 25' being a little stronger than 27.
- 26' is the line 4233, which is stronger than 28.
- 29' is the line 4191 much stronger than 27'.
- 28' is $\lambda 4154$, which is absent in the Geissler tube.
- 29' is $\lambda 4137$, which is stronger than 30.
- 31' is $\lambda 4122$, which is absent in the Geissler tube discharge.

Concluding Remarks.

The selective behaviour of the two spectra becomes evident from the above comparison. Among these observations a new band head in the neighbourhood of $\lambda 4500$ not mentioned by the previous observers has persistently appeared in our plates; as we could not detect any impurity excepting a trace of hydrogen, it appears that this band is due to the oxygen molecule. The band heads in the visible mentioned by other experimenters have also appeared on our plate. This matter is being investigated with the help of the Hilger Interchangeable Quartz Spectrograph of ten feet focus, and it is hoped to deal with that investigation in another communication.

Summary.

The spectrum of oxygen has been studied at a pressure of 0.2 to 0.3 mm. in a Geissler tube and in a special type of quartz discharge-tube. A striking differential behaviour in the nature of the two spectra was observed and a few striking differences are summarised above. In addition to this a new band head is observed in the neighbourhood of $\lambda 4500$. The structure of this band is being investigated with the help of the Hilger Interchangeable Quartz Spectroscope of ten feet focus.

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LXVIII. Scattering of Thorium C'' γ -radiation by Radium G and Ordinary Lead. By W. KUHN, Ph.D. (Heidelberg)*.

Introduction.

THE question was put forward some time ago whether, corresponding to an emission of monochromatic γ -rays by atomic nuclei, there should also exist a selective absorption of these rays. This would be in close analogy, *e. g.*, with the absorption of the D-lines by non-luminous sodium vapour. If one carries this analogy somewhat further, it is easy, with the aid of thermodynamical considerations†, to obtain an estimate of the order of magnitude of the absorption coefficients which might be found when atomic nuclei are irradiated with γ -rays of the proper frequencies. If N_0 be the number of atoms in unit volume, λ the wave-length of the radiation in question, g_0 and g_1 the statistical weights of the normal and excited states of the nucleus, the maximum value of the absorption coefficient in an undisturbed line would be expected to be

$$\frac{1}{d} \log_e \frac{I_0}{I} = \epsilon = \frac{g_1}{g_0} \frac{N}{2\pi} \lambda^2. \quad . \quad . \quad . \quad (1)$$

By introducing for N the value 3×10^{22} , which corresponds to the density of solid lead, and taking λ equal to 10 X-units, ϵ will come out about 50. This would be about one

* Communicated by Dr. J. Chadwick, F.R.S.

† W. Kuhn, *Zeits. f. Phys.* xliii. p. 56 (1927).

hundred times as large as the absorption coefficient due to the scattering of γ -rays by the electrons in the optical and X-ray levels of the same substance.

It will be seen, however, that the assumption of an undisturbed line is not satisfied under experimental conditions which can be attained in the laboratory. The observable absorption will then depend on the natural half-width of the line and the magnitude of the disturbing factors. As the half-width depends mainly on the charge and mass of the emitting particle, it is clear that a measurement of nuclear absorption might give us some information about the origin of the γ -rays and the circumstances accompanying their emission.

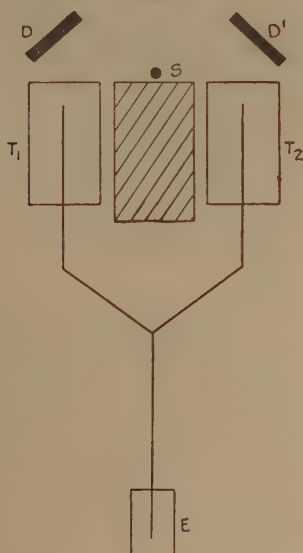
Instead of measuring the absorption, the scattering of thorium C'' γ -radiation by radium G and by ordinary lead has been compared. According to Aston * ordinary lead contains about 50 per cent. of isotope 208. The latter may be identified with thorium D, the end-product of the radioactive disintegration of thorium. Thorium D is formed from thorium C in two ways: two-thirds of the atoms of thorium C are transferred into thorium C' by a β -transformation and into thorium D by subsequent α -emission, while the remaining third of the thorium C-atoms emit an α -particle first, a transformation which leads to thorium C''. The thorium C'' nuclei finally transform into thorium D by a β -transformation followed by γ -ray emission. This γ -emission is thus the last step in this branch of the radioactive processes. It is therefore possible that some γ -lines of thorium C'', namely, those which are combinations of excited states with the normal state of thorium D, are resonance lines. Assuming that the nuclei of thorium D formed from thorium C in the two ways mentioned are all identical, and identical with the isotope 208 of ordinary lead, we would expect that 50 per cent. of the atoms present in ordinary lead are capable of resonance in such a way that a part of the γ -radiation of thorium C'' would be absorbed by the nuclei of thorium D, and re-emitted afterwards. The secondary radiation from ordinary lead would be increased, both electrons and nuclei taking part in producing the scattering. In the case of the lead isotope radium G, however, no nuclear scattering of thorium C'' radiation should be expected.

* F. W. Aston, 'Nature,' cxx. p. 224 (1927).

Experimental Arrangement.

The arrangement chosen was the following. T_1 and T_2 (see fig. 1) are two ionization chambers, rectangular boxes (about $10 \times 10 \times 25$ cm.), covered on the outside with 2 mm. of lead except for the top, which is a plate of brass 2 mm. thick. To these chambers voltages of equal magnitude (40 v.) and opposite sign were applied, so that the currents balanced one another. An initial difference

Fig. 1.



in the natural leak was corrected with the aid of a small subsidiary radioactive source, placed near one of the chambers. Thus the Compton electrometer E did not acquire a charge. A radioactive source S, *e.g.*, a tube containing radiothorium, is then placed near the top between the ionization chambers. The latter are screened from direct radiation by about 5 cm. of lead. In front of each ionization chamber glass dishes D and D' (diameter 8 cm.) could be placed. They had exactly the same size, and could be interchanged. Their position is reproducible with great accuracy, it being determined by a wooden

frame fastened with wax to the ionization chambers T_1 and T_2 . One of the dishes contained 126 g. of ordinary lead chloride, the other the same amount of radium G chloride*. The chloride was firmly pressed down into the dish and fixed in position by a plain wooden disk.

The γ -radiation from the radiothorium source falls through the bottom of the dishes on the layer of RaGCl_2 or PbCl_2 . The secondary radiation produced there will fall into the ionization chambers. By shifting the source by means of a screw, a position can be obtained where the currents through the chambers again very nearly cancel. The dishes with the ordinary lead chloride and the radium G chloride are then interchanged. A current different from the previous one will now flow to the electrometer. This difference can be due (1) to a real difference in the scattering power of the isotopes of lead; (2) to a geometrical irregularity in the arrangement of the substance inside the dish; (3) to differences concerning the dishes or the quantity of material used; (4) to the radioactivity of the uranium lead preparation, due to radioactive products separated with it.

The disturbing points (2) to (4) can most easily be eliminated by substituting for the radiothorium source a radium source of equal strength. In fact a nuclear resonance should not be expected at all with a radium source, either in radium G or in ordinary lead, while the factors (2) to (4) should remain unchanged. Therefore, if *a nuclear resonance of thorium D for the γ -radiation of thorium C" were present, we should find the difference in current observed for the two positions of the scatterers more in favour of the ordinary lead when a radiothorium source is used than when a radium source is used.*

* The author wishes to express his thanks to the Union minière du Haut Katanga, Brussels, from which he has obtained a preparation of RaGCO_3 . The atomic weight of the RaG has been determined by Prof. W. Hieber, Chemical Institute, University of Heidelberg, with the assistance of Messrs. Ries, Martin, and Eichel. The method consisted in recrystallizing the chloride, following the prescriptions of Hönigschmidt, and comparing the density with the density of ordinary lead chloride, purified in a similar way. The density of our RaGCl_2 was, at 25° , 5.8788 ± 0.0007 , while the density of PbCl_2 was 5.9034 ± 0.001 . Hence it follows that the atomic weight of our uranium lead was 206.04. Our preparation was thus practically pure isotope, 206.0. The author wishes to express his thanks, too, for the careful carrying out of this determination.

Experimental Result.

No such effect could be found, although about 100 curves (time against electrometer deflexion) were obtained and studied. In more detail the results were the following :—

(a) The current produced in one ionization chamber by the adjacent scattering dish (*e. g.*, in chamber T₁ by dish D, fig. 1) gave an electrometer deflexion of 570 mm./min. It was the same whether the radium or the radiothorium source was used.

(b) The current produced by the radioactivity of the uranium lead itself corresponded to 10 mm./min., or about 2 per cent. of the current due to the secondary radiation in the experiment.

(c) The current produced by the scattered radiation from ordinary lead exceeded the current produced by the scattered radiation from radium G by

17.6 \pm 1.5 mm./min. in the case of a RdTh source, and by
18.3 \pm 1.5 mm./min. „ „ Ra „

The ordinary lead thus apparently scattered both the thorium C'' γ -radiation and the radium γ -radiation more than did uranium lead. This is probably due to a different distribution of the chlorides inside the dishes (point (2) of the above-mentioned possibilities). The difference between the results with radiothorium and radium sources (18.3—17.6=0.7 mm./min.) is certainly less than the sum of the possible errors (3 mm./min. =0.5 per cent. of the total current). It can therefore be considered as proved that *the scattering of the γ -radiation of radiothorium (in equilibrium with thorium C'') by the thorium D nuclei present in ordinary lead is at least 200 times smaller than the electronic scattering in lead.*

Discussion.

We shall now discuss the possible theoretical meaning of this result. As the effect was a negative one, we shall be able only to exclude certain possibilities ; but even this may have some interest.

Assumption.—In order to make the problem more definite, we shall assume that one “resonance line” in

the spectrum of thorium C'' has the intensity 1, and can be absorbed. Its wave-length may be 30 X.U. Further, we assume that there are nine other lines, each of intensity 1, and which are not resonance lines.

The following remarks may be made about this assumption. The γ -radiation of radiothorium in equilibrium, which was used in the experiment, contains the soft γ -radiations of radiothorium, thorium B, thorium C, and the comparatively very hard γ -radiation from thorium C''. The resonance lines, if present, are lines from thorium C'', and might therefore very well have a shorter wave-length than what has been assumed. The further discussion will show that the assumption of a very hard resonance line (about 8 or 10 X.U.) would really lead to a satisfactory explanation of the experiment.

1. *The case of undisturbed lines.*—If the emission, as well as the absorption line, were undisturbed, we should expect a maximum absorption coefficient in pure thorium D of about $\epsilon_{\max.} = 500$. In ordinary lead, which only contains 50 per cent. of thorium D, this reduces to $\epsilon_{\max.} = 250$. In a layer of about 3 mm. of solid lead this line would have been completely absorbed and re-emitted. The non-resonance lines, for which the scattering coefficient may be assumed equal to 0.3, would in the same layer lose the $(1 - e^{-0.3 \times 0.3})$ th part, or about 10 per cent. of their original intensity, by scattering. The scattered light would have an intensity 1 from resonance scattering and an intensity $9 \times 0.1 = 0.9$ from electronic scattering. The resonance would thus double the apparent scattering power of the substance. This case is certainly not present in our experiment.

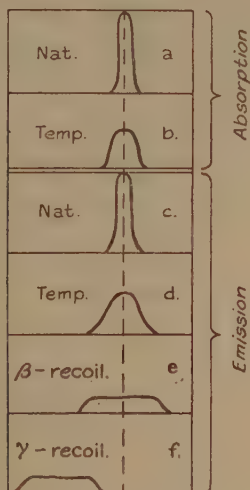
2. *General discussion of possible disturbances.*—It has already been mentioned that the effective absorption may be altered if the absorption or emission line is disturbed. Three such disturbances will be considered. Their influence on a narrow absorption and emission line is shown in fig. 2.

The first disturbing effect may be the temperature agitation. At room-temperature it causes (by Doppler effect) a broadening of the line ($\delta\nu_T = 1.5 \times 10^{14}$ sec.⁻¹). This will affect the absorption and emission line in the same way (*cf.* fig. 2, *b* and *d*).

Two further influences will change the emission line only : they may reduce the amount of absorption considerably. Before emitting rays, the atoms of thorium C'' have shot out a β -particle, and thereby suffered a recoil. Assuming the velocity of the β -particle to be about 0.9 that of light, the emission line will show an additional broadening, $\delta\nu_\beta = 1.5 \times 10^{15} \text{ sec.}^{-1}$ (cf. fig. 2, e). Thus even in the case of a "resonance line" only a part of the emitted light can be absorbed.

The third influence, reducing the absorption, arises from the emission process of the γ -rays. The emitting atom will

Fig. 2.



suffer a recoil due to projection of the γ -ray. The wavelength of the radiation is thereby shifted to the red ; the emission line is displaced relative to the absorption line (fig. 2, f). In our example the shift would be $\delta\nu_\gamma = 2 \times 10^{14} \text{ sec.}^{-1}$. It is thus possible that by a large γ -shift the whole emission line is brought out of the absorption region.

3. *Significance of the origin of the γ -rays for the resultant disturbance.*—The extent to which these three disturbances will really affect the absorption obviously depends on the natural width of the undisturbed line and thereby of the

origin and mechanism of the γ -ray emission. If the natural half-width is very narrow, the disturbances will be able to change the absorption effect completely. A small natural width ν means a long duration τ of the emission process, since these two magnitudes are connected by the relation

$\tau = \frac{1}{2\pi\nu}$, which is a simple geometrical consequence of the

wave-theory of light. A long duration of the emission process again means a small energy emission in unit time, and therefore a small electric moment connected with the motion inside the nucleus which gives rise to the γ -emission. In classical theory and in wave mechanics the mean time of duration of an emission process is determined in the same way (formulae (2) and (3)) if the charge, frequency, and (reduced) mass of the system is given. If we therefore construct any model of a γ -emitting nucleus, and assume that the model may be described by the help of quantum mechanics (some successful attempts have been made recently), we should be able to predict, as far as the order of magnitude is concerned, the width of the γ -lines.

If we seek to devise a model which will provide the fluctuating electric moment to which we attribute the emission of the γ -rays, we must suppose that some constituents of the nucleus are in relative motion to other constituents which have a different specific charge. Three especially simple possibilities present themselves. The electric moment might be due (a) to an electron; (b) to a proton; (c) to a helium nucleus moving as an individuum inside the heavy nucleus. For these cases the width of the γ -lines will be estimated and its effect on the observable absorption discussed.

(a) *Case of γ -rays due to an electron.*—In the case where the γ -rays were due to electrons bound inside the heavy nucleus, we should expect a half-width ν' , given in order of magnitude by

$$\nu' = \frac{4\pi e^2 \nu^2}{mc^3} f, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where f is a number somewhat smaller than unity. By introducing for e^2 and m the values characteristic for the electron, we get $\nu' \simeq 10^{18} \text{ sec.}^{-1}$. The natural width would be about 1000 times larger than the disturbances. The absorption phenomenon would be that of an undisturbed

line. This possibility, and thereby the electronic origin of the γ -rays, must consequently be excluded. The argument is in agreement with conclusions drawn from the polarizability* of nuclei and, according to Ellis, from the homogeneity† of the γ -rays.

(b) *Case of γ -rays due to protons.* The half-width to be expected if the γ -rays are emitted by protons can, in a rough approximation, be calculated from (2). It is not quite correct, because in the emission process we have neglected the contribution to the total electric moment which is due to the motion of the heavily-charged residual nucleus. This contribution (quite negligible for intensity questions in the Bohr hydrogen atom) becomes important because it is of the same order of magnitude as the moment due to the motion of the proton or α -particle which we suppose to be responsible for the γ -radiation. The correction will be particularly important in the case where the α -particle emits the γ -radiation.

If a particle of mass m and charge ze performs a harmonic motion together with another particle of mass M and charge Ze , the energy emission $\frac{dE}{dt}$ corresponding to the component of motion along the x -axis will depend on the acceleration of the electric moment m , namely,

$$\frac{dE}{dt} = \frac{2}{3} \frac{\ddot{m}^2}{c^3} = \frac{2}{3} \frac{e^2}{c^3} (z\ddot{x}_m + Z\ddot{x}_M)^2 = \frac{2}{3} \frac{e^2}{c^3} z^2 \ddot{x}_m^2 \left(1 - \frac{Z}{z} \frac{m}{M}\right)^2.$$

From this we see that the true emission is smaller by the factor $\left(1 - \frac{Z}{z} \frac{m}{M}\right)^2$ than the emission present if the motion of the residual nucleus were neglected. For that reason the half-width of the line will be reduced by the same factor, and consequently will be

$$\nu' = \frac{4\pi e^2 \nu^2 z^2}{mc^3} \left(1 - \frac{Z}{z} \frac{m}{M}\right)^2 \cdot f. \quad . \quad . \quad . \quad (3)$$

If we take m equal to the mass of the hydrogen atom, $z=1$, we find $\nu' = 2 \times 10^{14} \times f$. As f is rather smaller than unity, we may say $\nu' = 10^{14} \text{ sec.}^{-1}$.

The influences of the three disturbances on the absorption

* W. Kuhn, *Zeits. f. Phys.* xliv, p. 32 (1927).

† Cf. W. Kuhn, *Naturwissenschaften*, xvii, p. 431 (1929).

have now to be discussed. The temperature agitation broadens the line about three times and reduces the maximum absorption coefficient from 250 to 80. The β -recoil broadens the emission line further from 3×10^{14} to 3×10^{15} sec.⁻¹. We have mentioned that only a part of the emission line will now be absorbed. We shall therefore make an estimate of the value to which the absorption coefficient really falls at the edge of our emission line. As far as the temperature agitation is concerned, the absorption of the edge of the emission line will be negligible; it would

be of the order $\epsilon_{\text{max.}} = e^{-\frac{3 \cdot 10^{15}}{3 \cdot 10^{14}}}$. But it is well known that the decrease in intensity of an absorption or an emission line due to the "natural frequency-intensity distribution" of the line is, at large distances from the centre, much slower than the decrease due to the temperature agitation. We have now to find the absorption coefficient of a line at a distance $\nu_0 - \nu = 1.5 \times 10^{15}$ from the middle of the line, the maximum absorption coefficient of the undisturbed line being 250 and the natural half-width $\nu' = 10^{14}$. The value is to be obtained from the relation

$$\epsilon = \epsilon_{\text{max.}} \cdot \frac{\nu'^2}{4(\nu_0 - \nu)^2 + \nu'^2} = 250 \frac{1}{4 \cdot 15^2 + 1} \approx 0.28. \quad (4)$$

We see that even the edge of the emission line will be absorbed considerably.

The γ -shift will be smaller than the β -recoil broadening, namely, $\delta\nu_\gamma = 2.2 \times 10^{14}$. The greater part of the emission line will therefore be absorbed, and we should expect with our resonance line and our nine non-resonance lines a resultant nuclear effect about 50 per cent. as strong as the electronic scattering.

This result would even be true if we neglect the β -recoil broadening. According to Jacobsen*, it seems quite possible that a considerable time (about 10^{-5} sec.) elapses between the emission of the β -particle and the γ -radiation. In this case the γ -emitting atom would have lost the β -recoil velocity. The γ -recoil alone would now provide us with an emission line (temperature plus natural width) shifted relative to the absorption line by 2.2×10^{14} sec.⁻¹. Disregarding the temperature agitation, we find the absorption coefficient at the centre of the shifted line $\epsilon \approx 250 \frac{1}{4 \cdot 2^2} \approx 16$.

* J. C. Jacobsen, 'Nature,' cxx. p. 870 (1927).

The γ -shift brings the emission line away from the maximum absorption, but still leaves it in a region where it will be completely absorbed. *Thus in all cases which can be considered under the assumption that a proton emits the γ -radiation, we expect a nuclear effect which is much stronger than is allowed by the experiments.*

(c) *Case of γ -rays due to helium nuclei.*—In order to find the half-width of the emission line when a helium nucleus is supposed to emit the γ -rays, we have in formula (3) to put $z=2$ and to take $m=4$, the mass of the helium atom. The half-width then becomes $\nu' \simeq 2 \times 10^{13} \times f$. Taking again for f a value about 0.5, we have $\nu' = 10^{13} \text{sec.}^{-1}$. This value is ten times smaller than the value obtained for a proton as emitter of the radiation.

The reduction is due to the fact that the specific charge for the α -particle is nearly equal to that of the residual nucleus. If the two were exactly equal, the half-width would be infinitely small, the duration of the emission process infinitely long, because there would then, to a first approximation, be no change in the electric moment of the system, and therefore no radiation emission.

Quite in analogy to the previous treatment, we find that the temperature agitation brings the maximum absorption coefficient down to 8, while the β -recoil broadens the emission line. The edge of the emission line will no longer be absorbed; only the centre of the line (about 30 per cent.) remains absorbable. In fact, for the edge of the line we

find the absorption coefficient $\varepsilon \simeq 250 \frac{1}{4 \cdot 150^2} \simeq 0.003$. As

the γ -shift is smaller than the β -broadening, we expect in this case an apparent nuclear scattering only 30 per cent. of the electronic scattering.

If we, on the other hand, assume that the γ -emission follows the β -emission after more than 10^{-10} sec., the β -recoil broadening will be missing, and the emission line will fall to a place of the absorption curve where the

absorption coefficient would be $\varepsilon \simeq 0.16 = \frac{250}{4 \times 20^2}$. The

energy absorbed and scattered by a layer of 3 mm. will be $1 - e^{-0.3 \times 0.16} \simeq 0.05$, or about 5 per cent. of the electronic scattering of the lines. This amount reduces to 1 per cent. if we assume that the resonance line has a wave-length of

only 10 X.U., and would reduce to 0.25 per cent. if we had taken for f the value 0.25 instead of 0.5.

Summary.

We might expect a nuclear resonance of thorium D nuclei for some γ -lines of thorium C''. In order to test its existence, the scattering of thorium C'' γ -radiation by the lead isotope radium G and by ordinary lead has been compared.

It was found that the nuclear effect produced in ordinary lead by the γ -radiation of radiothorium in equilibrium with thorium C'' is at least 200 times smaller than the electronic scattering.

In explaining this negative result we should get into serious difficulties if we assumed that the γ -rays were emitted by electrons or by protons. The difficulties are smaller, and the expected effect falls within the limit of our experimental error, if we assume that :

1. The γ -rays are emitted by helium nuclei.
2. A time-interval of about 10^{-10} sec. or more elapses between the emission of the β -rays and the emission of the γ -rays. Some evidence of such a time-interval has previously been given by Jacobsen.
3. The resonance line must, in the case of thorium D, have a rather short wave-length (ca. 10 X.U. or less).
4. The movements of the α -particle cause the residual nucleus to move in such a way that the centre of gravity is at rest.

It is hardly necessary to emphasize that these conclusions have been drawn on the basis of a negative experimental statement. It is, of course, also possible that entirely new points of view are valid in the case of the nucleus ; but it may be interesting to see that the present state of the experiments does not yet make a fundamental change in our aspects necessary.

The experiment has been carried out in the Cavendish Laboratory, Cambridge. I wish to thank Prof. Sir E. Rutherford and Dr. J. Chadwick for the opportunity they gave me, and to Mr. G. T. P. Tarrant for experimental help during the investigation.

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LXIX. *Classical and Modern Electromagnetic Theories.*
By A. PRESS*.

SUMMARY.

A NUMBER of outstanding formulæ characterize the Restricted Relativity Theory of Prof. Albert Einstein. Notably a set of formulæ made use of by him is that of the Lorentz Transformation, according to which

$$T = \beta \left(t - \frac{vx}{c^2} \right); \quad X = \beta(x - vt).$$

It is shown that if account is taken of the two Fresnelian types of ætheric media, the one condensed after the manner of Stokes near atomic nuclei and forming the atomic diameters, the other being the normal æther between atoms, then the following Classical Formulæ obtain, viz. :—

$$T_1 = t - \frac{vx}{c^2}; \quad X_1 = \frac{1}{\beta}x - vt.$$

Again there is the formula according to which the non-Newtonian composition of velocities for electromagnetic (*i. e.*, light) waves is given by

$$\mathbf{w} = \frac{\mathbf{u} + \mathbf{v}}{1 + \frac{\mathbf{u}\mathbf{v}}{c^2}}.$$

This also is shown to follow from the nature of the atomic atmospheres already outlined and discussed in the author's previous paper, published in the *Phil. Mag.*, Oct. 1925, p. 809. The reconciliation then appears to be practically complete.

Later it is shown that for moving material dielectrics, using the above ideas of condensed and normal æthers, Heaviside's Wave-speed Mathematics, given in his 'Electromagnetic Theory,' iii. p. 45, can be clearly pictured. Thus the electromagnetic equations for moving dielectrics become

$$\begin{aligned} \frac{d\mathbf{D}}{dt} &= \text{curl} \{ \mathbf{h} - \kappa \mathbf{V} \mathbf{D} \mathbf{v} \}, \\ \frac{d\mathbf{h}}{dt} &= - \frac{c^2}{\mu k} \cdot \text{curl} \left\{ \mathbf{D} - \frac{\kappa(k\mu)}{c^2} \mathbf{V} \mathbf{v} \mathbf{h} \right\}. \end{aligned}$$

* Communicated by the Author.

As against the latter, using the Heaviside methods of analysis, these are equivalently expressed by the equations

$$\begin{aligned}\text{curl}(\mathbf{h} - \mathbf{V}\mathbf{D}\mathbf{q}) &= \dot{\mathbf{D}} = \text{curl}(\mathbf{h} - \kappa\mathbf{V}\mathbf{D}\mathbf{u}) \\ -\text{curl}(\mathbf{E} - \mathbf{V}\mathbf{w}\mathbf{B}) &= \dot{\mathbf{B}} = -\text{curl}(\mathbf{E} - \mathbf{V}\mathbf{w}\mathbf{B}).\end{aligned}$$

These equations lead at once to the Fresnelian drag coefficient and to the non-Newtonian composition of velocities required by the Einstein relativistic ideas.

Turning next to an independent derivation of the fundamental equations of Lorentz, it is shown that the Trouton-Noble experiment falls into line because of the important limitation due to the divergence operator employed. Incidentally it also follows that the Wilson effect and the Röntgen current accord with the above equations.

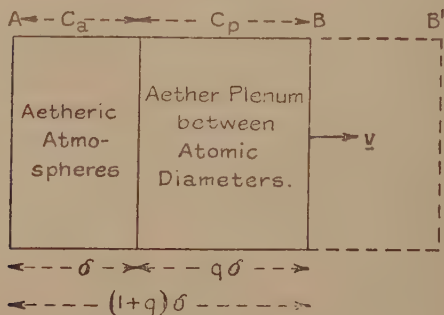
In the last section is discussed the Michelson-Morley experiments. The formulæ derived indicate that for air, at least, the effect should be null.

EFFECTIVE OPTICAL TIMES AND DISTANCES IN CLASSICAL AND RELATIVITY THEORIES.

ON the theory of æther-condensation atmospheres produced by the presence of atomic nuclei in the æther, two time-periods T_0 and T_v are indicated. An electromagnetic disturbance travelling through a material dielectric of length

$$x = AB, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Fig. 1.



with regard to A as the origin, requires a time T_0 if the body is at rest relative to the normal uncondensed æther. It, however, requires a different time T_v if the material of

length $x = AB$ is moving forward with velocity \mathbf{v} in the same direction as the propagated electromagnetic wave. This is because, in travelling forward, the end-point B in the meantime reaches a point B' in the normal æther. The time T_0 is given by the expression

$$T_0 = \frac{\delta}{c_a} + q \frac{\delta}{c_p} = \frac{\delta}{c_a c_p} \{c_p + q c_a\}, \quad . . . \quad (2)$$

where we have that

c_a = velocity of light through the ætheric condensation atmospheres,

c_p = velocity through the normal interatomic æther plenum.

On the other hand, for the T_v time the expression obtained is

$$T_v = \frac{\delta}{c_a} + \frac{q\delta + vT_v}{c_p + v} = \frac{\delta}{c_a c_p} \{c_p + q c_a + v\}, \quad . . \quad (3)$$

The ratio of the two time-periods is therefore given by

$$\left. \begin{aligned} T_v/T_0 &= 1 + \frac{v}{c_p + q c_a} \\ \text{and} \\ T_v &= T_0 + \frac{v}{c_p + q c_a} \cdot T_0. \end{aligned} \right\} \quad (4)$$

Yet from the figure we have that

$$x = AB = (1 + q)\delta. \quad \quad (5)$$

The definitions of the two times can also be taken as follows:—

$T_0 = t$ = optical time with body at rest ;

$T_v = T'$ = effective optical time with body in motion arising from differential motions due to the Fresnelian æthers.

Thus we can write

$$\left. \begin{aligned} t = T_0 &= \frac{x}{1 + q} \cdot \frac{c_p + c_a q}{c_a c_p}, \\ T' = t &+ \frac{vx}{(1 + q) c_a c_p}. \end{aligned} \right\} \quad (6)$$

For the bodily velocity \mathbf{v} , therefore, taken negatively or opposite to the propagational direction of the electromagnetic disturbance, we have

$$T' = t - \frac{vx}{(1 + q) c_a c_p}, \quad \quad (7)$$

2 X 2

which, of course, bears a distinct resemblance to the Lorentz Transformation T in Relativity Theory.

Calling c' the average velocity of propagation through the distance $(1+q)\delta$, with the body at rest relative to the æther, we can write

$$(1+q)\frac{\delta}{c'} = \frac{\delta}{c_a} + q\frac{\delta}{c_p},$$

$$1+q = \frac{c'}{c_a} + q\frac{c'}{c_p} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Introducing n_a as the refractive index of the atomic diameters, we have practically that

$$n_a = \frac{c}{c_a} \equiv \frac{c_p}{c_a} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It will be noticed that a possible distinction can be made between the c_p of the interatomic æther and the c of free space. Again, if n is the mean refractive index of the material medium as a whole (when the body is at rest relative to the æther) it will follow that

$$n = \frac{c}{c'} \equiv \frac{c_p}{c'} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The equation therefore becomes

$$1+q = \frac{n_a}{n} + q\frac{1}{n} ; \quad n_a - n = (n-1)q ;$$

$$1+q = \frac{n_a-1}{n-1} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The denominator of T' is transformable, as a consequence of the above, into the form

$$(1+q)c_a c_p \equiv \frac{n_a-1}{n-1} \cdot \frac{1}{n_a} \cdot c^2 \quad . \quad . \quad . \quad . \quad (12)$$

This means, with the understanding "at rest," we can assume for the respective refractive indices that

$$\left. \begin{aligned} \frac{n_a-1}{n-1} \cdot \frac{1}{n_a} &\equiv 1, \\ n_a &\equiv n \equiv 1. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (13)$$

We have, as a result, that

$$\underline{T' = t - \frac{vx}{c^2}} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The Lorentz Transformation and the Relativity Theory require that we write

$$T = \beta \left(t - \frac{vx}{c^2} \right). \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus the difference between T' on the Classical Theory and the T of Relativity Theory is a factor β , where

$$\beta^2 = \frac{1}{1 - \frac{v^2}{c^2}}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The latter involves terms of the second order only.

Treating now optical distances in the same manner, we have from the figure that the effective optical distance X is given by

$$X' = (1 + q)\delta + BB' = x + BB'. \quad . \quad . \quad . \quad (17)$$

The same reasoning as before has to be advanced. A light disturbance generated at A in the moving body not only has to pass through the sum total of ætheric atmospheres indicated by the length δ with respect to the actual (at rest) length AB , but, by virtue of the body moving forward with velocity v , traverses a normal æther distance $q\delta + BB'$, because the real end of the body B reaches the point B' in the meantime.

The addition BB' due to the motion of the body through the normal æther medium is given by

$$BB' = vT_v. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Thus it follows that

$$X' = x + vT_v = x + v \left(t - \frac{vx}{c^2} \right). \quad . \quad . \quad . \quad (19)$$

That is to say, on rearrangement of terms, we have

$$X' = \left(1 - \frac{v^2}{c^2} \right) x + vt. \quad . \quad . \quad . \quad . \quad (20)$$

Taking, therefore, v negatively, as before, we have as a consequence

$$\underline{X' = \frac{1}{\beta} x - vt.} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The Relativity Theory gives, however,

$$X = \beta(x - vt). \quad . \quad . \quad . \quad . \quad (22)$$

The difference between the optically effective value of X in the two systems is therefore of the second order.

PART II.

THE DIFFERENTIAL EQUATIONS OF ELECTROMAGNETIC THEORY.

Let the electrical displacement of Maxwell be represented by

$$\mathbf{d} = \mathbf{D} + \mathbf{D}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where \mathbf{D} represents a circuital displacement for all space due to electrization as defined by Heaviside, and \mathbf{D} represents a polar displacement due to electrification as defined by Heaviside. If, then, we operate with div and curl , it follows that

$$\text{div } \mathbf{d} = \text{div } \mathbf{D} = \rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\text{curl } \mathbf{d} = \text{curl } \mathbf{D}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Differentiating with respect to time, we have from (24)

$$\frac{d\rho}{dt} = \text{div } \frac{d\mathbf{D}}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Consider, on the other hand, the divergence of a vector $\rho \mathbf{u}'$, where \mathbf{u}' is the translational velocity of a charge density ρ across free space. We have

$$\begin{aligned} \text{div } \rho \mathbf{u}' &= \nabla \rho \mathbf{u}' = \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right) (\rho u_x \mathbf{i} + \rho u_y \mathbf{j} + \rho u_z \mathbf{k}) \\ &= \frac{\partial}{\partial x} (\rho u_x) + \frac{\partial}{\partial y} (\rho u_y) + \frac{\partial}{\partial z} (\rho u_z). \quad . \quad . \quad . \quad . \quad . \quad (27) \end{aligned}$$

Ordinarily, however, we shall also have (for the general case, mathematically)

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} \frac{dx}{dt} + \frac{\partial \rho}{\partial y} \frac{dy}{dt} + \frac{\partial \rho}{\partial z} \frac{dz}{dt}. \quad . \quad (28)$$

If, then, there is no change in the ionization occurring, we shall have

$$\frac{\partial \rho}{\partial t} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Thus, with the electrification constant,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial x} \frac{dx}{dt} + \frac{\partial \rho}{\partial y} \frac{dy}{dt} + \frac{\partial \rho}{\partial z} \frac{dz}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Given that the coordinates (x, y, z) pertaining to the location of a charge density ρ change with respect to time

relative to a fixed frame of reference (x', y', z') , we shall have

$$\left. \begin{aligned} u_x' &= \frac{dx}{dt}, \\ u_y' &= \frac{dy}{dt}, \\ u_z' &= \frac{dz}{dt}. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (31)$$

Thus, by means of (31) it follows that

$$\frac{d\rho}{dt} = u_x' \cdot \frac{\partial \rho}{\partial x} + u_y' \cdot \frac{\partial \rho}{\partial y} + u_z' \cdot \frac{\partial \rho}{\partial z} \dots \dots (32)$$

Equation (32) has now to be correlated with (27). Yet in order that (27) and (32) should be equivalent, we must specify

$$\left. \begin{aligned} u_x' &= f_x(y, z, t) \text{ and independent of } x, \\ u_y' &= f_y(x, z, t) \quad , \quad , \quad , y, \\ u_z' &= f_z(x, y, t) \quad , \quad , \quad , z. \end{aligned} \right\} \quad . \quad . \quad (33)$$

These are very serious limitations. Only when (33) are satisfied can we write (32) in the form

$$\frac{d\rho}{dt} = \frac{\partial}{\partial x}(\rho u_x') + \frac{\partial}{\partial y}(\rho u_y') + \frac{\partial}{\partial z}(\rho u_z') \dots \dots (27')$$

Thus, if we are considering a given distribution of ρ in space, then the velocity component u_x' of the charges plus and minus for the whole field must be independent of x , etc. Surely this is equivalent to regarding the movement of the whole aggregation of charges + and - as partaking of a rigid body movement. Thus the distance between neighbouring charges becomes invariable. The equation

$$\frac{d\rho}{dt} = \text{div } \rho \mathbf{u}' \dots \dots \dots (27'')$$

constitutes one of the "derived equations" of Lorentz (see Cunningham, 'Relativity,' p. 23). The limitations (33), however, are ignored, and would not permit of a Lorentzian type of "polarization," which is polar, and never circuital, in its displacement flux distribution. *It also explains the Trouton-Noble negative result.*

Equation (27''), with changed sign of \mathbf{u}' , is equivalent to

$$\text{div} \left\{ \frac{d\mathbf{d}}{dt} + \rho \mathbf{u}' \right\} = 0, \quad . \quad . \quad . \quad . \quad (28')$$

so that for the general case we can assume a circuital vector \mathbf{h} such that

$$\operatorname{div} \operatorname{curl} \mathbf{h} = 0, \quad . \quad . \quad . \quad (34)$$

and, combined with (28'), we have

$$\frac{d}{dt} \mathbf{d} + \rho \mathbf{u}' = \operatorname{curl} \mathbf{h}. \quad . \quad . \quad . \quad (35)$$

The latter constitutes one of the "fundamental equations" of Lorentz. Here, however, it is made a derived equation (Cunningham, *l. c.* p. 23).

Lemma.

Postulating now that in an electromagnetic field the velocity with which a lateral disturbance can be propagated forwardly is represented by c , we have for the magnetic effect \mathbf{h} in an x -direction

$$\mathbf{h} = \mathbf{h}_0 \cdot F(x - ct) = \mathbf{h}_0 F(\xi). \quad . \quad . \quad . \quad (36)$$

It would then follow, by differentiating,

$$\left. \begin{aligned} \frac{\partial \mathbf{h}}{\partial t} &= \mathbf{h}_0 \cdot \frac{dF}{d\xi} \cdot \frac{\partial \xi}{\partial t} = \mathbf{h}_0 \frac{dF}{d\xi} (-c), \\ \frac{\partial \mathbf{h}}{\partial x} &= \mathbf{h}_0 \frac{dF}{d\xi} \cdot \frac{\partial \xi}{\partial x} = \mathbf{h}_0 \frac{dF}{d\xi}, \\ \left. \begin{aligned} \frac{\partial \mathbf{h}}{\partial t} &= -c \frac{\partial \mathbf{h}}{\partial x}, \\ \frac{\partial^2}{\partial t^2} &= c^2 \frac{\partial^2}{\partial x^2}. \end{aligned} \right\} . \quad . \quad . \quad . \quad (37)$$

Operating now on (35), with curl , we have

$$\operatorname{curl} \frac{d}{dt} \mathbf{d} + \operatorname{curl} \cdot \rho \mathbf{u}' = \operatorname{curl}^2 \mathbf{h}. \quad . \quad . \quad . \quad (38)$$

Yet from (27'') $\rho \mathbf{u}'$ cannot have curl , since it already has divergence, and then note must be taken of (33). Thus, by (23), (38) reduces to

$$\operatorname{curl} \frac{d\mathbf{D}}{dt} = \operatorname{curl}^2 \mathbf{h}. \quad . \quad . \quad . \quad (39)$$

Vectorially, however, if \mathbf{h} is wholly a circuital vector, then the operator curl^2 reduces to $-\nabla^2$. That is, in this instance,

$$\operatorname{curl}^2 = -\nabla^2 = -\left(\mathbf{N} \frac{d}{dN}\right)^2 = -\frac{d^2}{dN^2} = -\frac{\partial^2}{\partial x^2}.$$

The equation (39) therefore becomes

$$\text{curl} \frac{d\mathbf{D}}{dt} = -\frac{\partial^2}{\partial x^2} \mathbf{h}. \quad . \quad . \quad . \quad . \quad (40)$$

For a progressive wave possibility in \mathbf{h} , therefore, according to (36) and (37), we have

$$\begin{aligned} \nabla^2 \mathbf{h} &= \frac{1}{c^2} \frac{d^2 \mathbf{h}}{dt^2}, \\ \text{curl} \frac{d\mathbf{D}}{dt} &= -\frac{1}{c^2} \frac{d^2 \mathbf{h}}{dt^2}, \\ \text{curl} \mathbf{D} &= -\frac{1}{c^2} \frac{d\mathbf{h}}{dt}. \quad . \quad . \quad . \quad . \quad (41) \end{aligned}$$

The two equations fundamental to electrodynamics, namely,

$$\left. \begin{aligned} \frac{d\mathbf{d}}{dt} + \rho \mathbf{u}' &= \text{curl} \mathbf{h}, \\ -\frac{1}{c^2} \frac{d\mathbf{h}}{dt} &= \text{curl} \mathbf{d}, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (42)$$

have been derived without requiring the introduction of the ideas of the electrical intensity \mathbf{E} and magnetic density \mathbf{B} .

Laws of Moving Dielectrics with Fresnel Correction.

Consider, in the first instance, a material dielectric system S of refractive index n at rest relative to the ætherial medium. A progressive wave of displacement is set up, and the equations to be satisfied are still the following:

$$\left. \begin{aligned} \frac{d\mathbf{D}}{dt} &= \text{curl} \mathbf{h}, \\ \text{curl} \mathbf{D} &= -\frac{1}{c^2} \frac{d\mathbf{h}}{dt}. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (43)$$

The term $\rho \mathbf{u}'$ is ignored, since progressive waves are in question.

Suddenly let a relative motion \mathbf{v} be produced of the material dielectric relative to the æther. Then will equations (43) need to be modified if ætheric reactions are assumed to take place by virtue of the relative motion between the æther and the material dielectric. Maxwell had already introduced a motional electric force \mathbf{e} given by

$$\mathbf{e} = \mathbf{V} \mathbf{v} \mathbf{B}. \quad . \quad . \quad . \quad . \quad (44)$$

Yet the circumstances are not quite the same; whereas Maxwell imagined the \mathbf{e} is set up by a conductor cutting across a magnetic field \mathbf{B} fixed in the æther, in the present case the \mathbf{B} (as well as the \mathbf{D}) were already travelling as progressive waves in the material dielectric when the latter was at rest with respect to the æther. It is the additional effect that is sought as the æther moves with respect to the dielectric, in which latter the progressive waves of \mathbf{D} and \mathbf{h} (or \mathbf{B}) already happen to find themselves.

Thus, with Fresnel (see Silberstein, 'Theory of Relativity,' p. 37), let the refractive index, or optical "density," of a material dielectric be explainable on the basis of a denser ætherial medium within the matter. In the writer's paper (*l. c.*) it was brought out that the atoms were to be conceived as atomic nuclei producing by their presence, in a gravitational or Stokesian sense, a condensed ætheric system of atmospheres about the nuclei wherever they may happen to be, whether at rest or in motion.

In reality, if δ_0 is the normal density of the free æther outside, then, with Fresnel, it is the excess density

$$\delta - \delta_0$$

that moves, or appears to move, with velocity \mathbf{v} , since it is this amount that is continually being produced by the presence of the atomic nuclei. The actual "quantity of movement" is therefore

$$(\delta - \delta_0)\mathbf{v}.$$

However, in terms of the over-all density δ we shall need to introduce a coefficient κ , since the waves will partly travel through the denser ætheric medium, and only in between times through the otherwise æther medium itself, filling the spaces between atoms. Thus, as explained in the paper above mentioned, if the nuclei carry their condensing power with them as they travel through space, then the only transport through the æther is that due to the travelling nuclei and not the atomic atmospheres which they produce as they move along. This suggests, of course, Dr. C. V. Burton's strain-figure theory already discussed by Heaviside in his 'Electromagnetic Theory,' i. Thus we need to write for the statistical or average effect

$$\left. \begin{aligned} (\delta - \delta_0)v &= \kappa \delta v, \\ \kappa &= 1 - \frac{\delta_0}{\delta}. \end{aligned} \right\} \dots \dots \dots (45)$$

But Fresnel assumed that the elasticities of the free and condensed æthers are the same. Thus we have that

$$n = \frac{\sqrt{\epsilon_0/\delta_0}}{\sqrt{\epsilon/\delta}},$$

$$\kappa = 1 - \frac{1}{n^2}. \quad . \quad . \quad . \quad . \quad . \quad (46)$$

From this point of view it is the condensed æther only that can be said to travel with respect to the free æther.

Provisionally, therefore, we can write, with κ as the slippage coefficient,

$$\mathbf{e} = \frac{D\mathbf{e}}{k_e} = \kappa \mathbf{V} \nabla \mathbf{B} = \left(1 - \frac{1}{n^2}\right) \mathbf{V} \nabla \mathbf{B}. \quad . \quad . \quad . \quad (47)$$

Similarly, for the electrical effect of moving media we may write

$$\mathbf{h}_1 = \kappa \mathbf{V} D \nabla. \quad . \quad . \quad . \quad . \quad . \quad (48)$$

The latter formula, by the way, agrees exactly with the requirements of the experimentally-determined Röntgen current, as given by Eichenwald (see Silberstein, *l. c.* p. 275). Given then that u is the velocity of propagation in the material medium when at rest relative to the æther, we have

$$u^2 = \frac{c^2}{\mu k}, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

and the equations become

$$\left. \begin{aligned} \frac{d\mathbf{D}}{dt} &= \text{curl} \{ \mathbf{h} - \kappa \mathbf{V} D \nabla \}, \\ \frac{d\mathbf{h}}{dt} &= -\frac{c^2}{\mu k} \text{curl} \left\{ \mathbf{D} - \frac{\kappa(k\mu)}{c^2} \mathbf{V} \nabla \mathbf{h} \right\}. \end{aligned} \right\} \quad . \quad . \quad (50)$$

The above, when checked, will be found to give the Fresnel dragging coefficient κ , where

$$\frac{w-u}{v} = \kappa = 1 - \frac{1}{n^2},$$

and w is the resultant velocity of the \mathbf{D} or \mathbf{h} wave in the material dielectric of the form

$$\mathbf{D} = \mathbf{D}' \sin(x - wt).$$

This will be gone into a little later. One thing is very clear, that where

$$n \equiv 1,$$

as in air, in which medium the Michelson-Morley-Miller experiments were conducted, practically no evidence of a difference in the moving-medium wave-velocity w as against the stationary-medium wave-velocity u should be found.

Alternative Fresnel Correction Derivation.

The two motional equations given by Heaviside in his 'Electromagnetic Theory,' i. p. 43, are as follows :

$$\mathbf{e} = V\mathbf{q}\mathbf{B}; \quad \mathbf{h} = V\mathbf{D}\mathbf{q}, \quad . \quad . \quad . \quad (51)$$

with \mathbf{q} as the velocity. (*The Heaviside notation will be used exclusively in this section.*)

In treating of the æther drag Heaviside (*l. c.* iii. p. 45) considers the case where two parallel and distinct electrical displacements are assumed, set up as a consequence of a single impressed force. Thus for the more general case, which can include the so-called "polarization" of Lorentz (in reality the latter's "polarization" is but a separation of charges), let

\mathbf{D}_0 = Maxwellian ætheric displacement,

\mathbf{D}_1 = second (including that of Lorentz), but always associated with the presence of matter.

Then can we write

$$\mathbf{D} = \mathbf{D}_0 + \mathbf{D}_1 = c\mathbf{E}. \quad . \quad . \quad . \quad (52)$$

(Note c is here the dielectric constant, and not the former velocity of light. The \mathbf{E} is the impressed electrical force.)

It is then assumed that we have

$$\mathbf{D}_0 = c_0\mathbf{E}; \quad \mathbf{D}_1 = c_1\mathbf{E};$$

$$\mathbf{D} = \mathbf{D}_0 + \mathbf{D}_1 = (c_0 + c_1)\mathbf{E} = c\mathbf{E}. \quad . \quad . \quad . \quad (53)$$

Similarly we have for the magnetic case

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1 = \mu\mathbf{H} = \mu_0\mathbf{H} + \mu_1\mathbf{H}. \quad . \quad . \quad . \quad (54)$$

Thus does it follow that

\mathbf{B}_0 = magnetic density set up in free space.

\mathbf{B}_1 = magnetic density set up as a consequence of the presence of matter (ferromagnetic effect).

Now in order to give tangibility to Heaviside's otherwise very obscure reasoning regarding his velocities \mathbf{q} and \mathbf{w} , the Ætheric Atmosphere Theory of Atoms (*l. c.*) lends a

helping hand. Thus the propagational velocity in the matter as a whole will be influenced by the velocity through the atomic diameters as against the different velocity through the free æther between atoms. Thus, assuming

$$\left. \begin{aligned} u &= \text{bodily velocity of the matter concerned,} \\ &\text{then} \\ u + v_a &= \text{resultant propagational velocity through} \\ &\text{the atomic atmospheres, where} \\ v_a &= \text{the propagational velocity with the matter} \\ &\text{at rest relative to the æther.} \end{aligned} \right\} \quad (55)$$

In the free æther of the intervening spaces we have

$$v = \text{velocity of propagation in the æther itself.}$$

A wave travelling through the matter, therefore, would thus have a velocity intermediate between v and $u + v_a$.

With the above visualization, let

$$\left. \begin{aligned} q_0 &= \text{effective velocity linked with the dielectric} \\ &\text{displacement } D_0, \text{ and giving} \\ VD_0 q_0 &= h_0 = \text{motional magnetic intensity set up.} \\ &\text{The } q_0 \text{ would then correspond to a} \\ &\text{space averaging for the inter- and} \\ &\text{intra-atomic spaces.} \\ q_1 &= \text{effective velocity linked with the dis-} \\ &\text{placement } D_1, \text{ and giving} \\ VD_1 q_1 &= h_1 = \text{motional magnetic intensity set up.} \\ &\text{The } q_1 \text{ here corresponds to the} \\ &\text{space averaging necessary due to} \\ &\text{the localization of the } D_1 \text{ displace-} \\ &\text{ment itself.} \end{aligned} \right\} \quad (56)$$

Thus both the q_0 and q_1 are really functions of the translational velocity u with which the matter moves relative to the æther. Similar equations will therefore follow for the magnetic motionals.

If, then, H and E are the respective forces set up by a wave when the body is at rest, then correspondingly the forces when the body moves with velocity u will be

$$\left. \begin{aligned} H &-(h_0 + h_1), \\ E &-(e_0 + e_1). \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (57).$$

The equations for a moving dielectric should then be

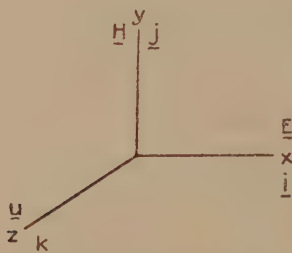
$$\left. \begin{aligned} \text{curl} \{ \mathbf{H} - (V D_0 \mathbf{q}_0 + V D_1 \mathbf{q}_1) \} &= \dot{\mathbf{D}}, \\ -\text{curl} \{ \mathbf{E} - (V w_0 \mathbf{B}_0 + V w_1 \mathbf{B}_1) \} &= \dot{\mathbf{B}}. \end{aligned} \right\} \quad (58)$$

It is the latter equations that will be shown not only to give the Fresnel drag coefficient, but actually to lead to the equations (50).

The Fresnel Wave-speed and Final Form of Electromagnetic Equations.

To investigate for a plane wave travelling in the moving body with a velocity \mathbf{U} relative to the stationary æther, the

Fig. 2.



form of the function would depend on the expression

$$\left. \begin{aligned} &f(z + Ut), \\ \text{giving } \frac{\partial}{\partial z} &= \frac{1}{U} \frac{\partial}{\partial t}. \end{aligned} \right\} \quad (59)$$

Thus we can set \mathbf{E} in the direction of the unit vector \mathbf{i} (axis of x), with \mathbf{H} along \mathbf{j} , and the wave itself travelling parallel to \mathbf{u} or the axis of \mathbf{k} .

The curl equations become, with

$$\begin{aligned} \mathbf{V} \nabla &= \text{curl} = \frac{\partial}{\partial z} \cdot \mathbf{k}, \\ \frac{\partial}{\partial z} \{ \mathbf{H} + q_0 D_0 + q_1 D_1 \} &= U \frac{\partial \mathbf{D}}{\partial t}, \\ \frac{\partial}{\partial z} \{ \mathbf{E} + w_0 B_0 + w_1 B_1 \} &= U \frac{\partial \mathbf{B}}{\partial t}. \end{aligned}$$

That is, we have the equations of condition,

$$\left. \begin{aligned} \mathbf{H} + q_0 \mathbf{D}_0 + q_1 \mathbf{D}_1 &= \mathbf{U} \mathbf{D}, \\ \mathbf{E} + w_0 \mathbf{B}_0 + w_1 \mathbf{B}_1 &= \mathbf{U} \mathbf{B}. \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (60)$$

However, it is easy to see that the latter can be greatly simplified, for we note that

$$q_0 \mathbf{D}_0 + q_1 \mathbf{D}_1 = (q_0 c_0 + q_1 c_1) \mathbf{E}.$$

Since we can also write, for convenience, that

$$q_0 c_0 + q_1 c_1 = qc,$$

and already by (53) we have

$$c = c_0 + c_1,$$

the definition of q is therefore

$$q = \frac{q_0 c_0 + q_1 c_1}{c} = \frac{c_0}{c} q_0 + \frac{c_1}{c} q_1. \quad \cdot \quad \cdot \quad \cdot \quad (61)$$

The velocities q , q_0 , q_1 are then so related that we can write

$$\mathbf{q} \mathbf{D} = (c_0 \mathbf{q}_0 + c_1 \mathbf{q}_1) \frac{\mathbf{D}}{c} = (c_0 \mathbf{q}_0 + c_1 \mathbf{q}_1) \mathbf{E}. \quad \cdot \quad \cdot \quad (62)$$

Thus but one effective velocity q need be considered in conjunction with but a single displacement \mathbf{D} instead of the two before employed.

Similarly therefore we have

$$\mathbf{w} \mathbf{B} = (\mu_0 \mathbf{w}_0 + \mu_1 \mathbf{w}_1) \frac{\mathbf{B}}{\mu} = (\mu_0 \mathbf{w}_0 + \mu_1 \mathbf{w}_1) \mathbf{H}. \quad \cdot \quad (63)$$

The corresponding equations in w are therefore

$$w = \frac{w_0 \mu_0 + w_1 \mu_1}{\mu}; \quad \mu = \mu_0 + \mu_1. \quad \cdot \quad \cdot \quad (64)$$

The curl equations become considerably simplified, for we have equivalently that

$$\left. \begin{aligned} \text{curl}(\mathbf{H} + \mathbf{V} \mathbf{D} \mathbf{q}) &= \dot{\mathbf{D}} = \text{curl}(\mathbf{H} - \mathbf{h}), \\ \text{curl}(\mathbf{E} - \mathbf{V} \mathbf{w} \mathbf{B}) &= -\dot{\mathbf{B}} = \text{curl}(\mathbf{E} - \mathbf{e}). \end{aligned} \right\} \quad \cdot \quad \cdot \quad (65)$$

These, however, are not in the final form required.

Turning to the relation of wave-speed U in terms of q and w we have from (60) that

$$\begin{aligned} \mathbf{H} + q \mathbf{D} &= \mathbf{U} \mathbf{D}; & \mathbf{H} &= (\mathbf{U} - q) \mathbf{D}; \\ \mathbf{E} + w \mathbf{B} &= \mathbf{U} \mathbf{B}; & \mathbf{E} &= (\mathbf{U} - w) \mathbf{B}. \end{aligned}$$

Eliminating \mathbf{E} , it follows that

$$\mathbf{H} = (\mathbf{U} - q)c\mathbf{E} = (\mathbf{U} - q)c(\mathbf{U} - w)\mu\mathbf{H} = \mu c(\mathbf{U} - q)(\mathbf{U} - w)\mathbf{H}.$$

It follows in consequence that

$$1 = \mu c(\mathbf{U} - q)(\mathbf{U} - w). \quad . \quad . \quad . \quad (66)$$

Since, now, the velocity of propagation \mathbf{v} with the medium at rest relative to the æther is given by

$$\frac{1}{\mu c} = v^2. \quad . \quad . \quad . \quad (67)$$

we have, solving for \mathbf{U} in (66), that

$$\begin{aligned} \mathbf{U}^2 - (w + q)\mathbf{U} &= v^2 - wq, \\ \mathbf{U} &= \frac{1}{2}(w + q) + \sqrt{v^2 + \frac{1}{4}(w - q)^2} \\ &\equiv v + \frac{1}{2}(w + q). \quad . \quad . \quad . \quad (68) \end{aligned}$$

If, then, w and q are both zero (medium at rest), then \mathbf{U}_0 equals v . Thus \mathbf{U} is the velocity of propagation for a moving dielectric as against the rest value \mathbf{U}_0 .

The change of wave-speed from what it would be with a material dielectric stationary is therefore

$$\mathbf{U} - v \equiv \frac{1}{2}(w + q). \quad . \quad . \quad . \quad (69)$$

Noting, however, that both w and q are functions of the translatory velocity \mathbf{u} , we can write

$$\left. \begin{aligned} \mathbf{w} &= \kappa_w \cdot \mathbf{u}, \\ \mathbf{q} &= \kappa_q \cdot \mathbf{u}. \end{aligned} \right\} \quad . \quad . \quad . \quad (70)$$

We then have that

$$\frac{\mathbf{U} - v}{u} = \kappa = \frac{1}{2}(\kappa_w + \kappa_q), \quad . \quad . \quad . \quad (71)$$

where κ is Fresnel's dragging coefficient. If, then, we set

$$\left. \begin{aligned} w &= q; \quad \kappa_w = \kappa_q = \kappa; \\ \frac{\mathbf{U} - v}{u} &= \kappa = 1 - \frac{1}{n^2}; \end{aligned} \right\} \quad . \quad . \quad . \quad (72)$$

where n is the refractive index. Making, therefore, use of (70) and (72), it follows that (65) becomes

$$\left. \begin{aligned} \dot{\mathbf{D}} &= \text{curl} \{ \mathbf{H} - \kappa \mathbf{V} \mathbf{D} \mathbf{u} \}, \\ \dot{\mathbf{B}} &= -\text{curl} \{ \mathbf{E} - \kappa \mathbf{V} \mathbf{w} \mathbf{B} \}, \end{aligned} \right\} \quad . \quad . \quad . \quad (50')$$

which are really equations (50)!

*Classical Non-Newtonian Composition of Velocities
for Moving Dielectric Media.*

The two equations previously developed for moving media were as follows :

$$\left. \begin{aligned} \frac{d\mathbf{D}}{dt} &= \text{curl} \{ \mathbf{h} - \kappa \mathbf{V} \mathbf{D} \mathbf{v} \}, \\ \frac{d\mathbf{h}}{dt} &= -\frac{c^2}{\mu k} \text{curl} \left\{ \mathbf{D} - \frac{\kappa k \mu}{c^2} \mathbf{V} \mathbf{v} \mathbf{h} \right\}, \end{aligned} \right\} \dots \dots (50)$$

in which the slippage coefficient κ is given by

$$\kappa = 1 - \frac{1}{n^2} = \frac{w-u}{v} \dots \dots \dots (73)$$

In the latter formula we have

n = refractive index,

w = wave-propagational velocity in moving dielectric,

u = wave-propagation velocity in the same dielectric
at rest with respect to the æther, and

v = translational velocity of the dielectric.

In the Michelson-Morley experiment, where for air we have

$$n \equiv 1,$$

it was shown that

$$\kappa \equiv 0,$$

and therefore, quite irrespective of the direction of v with respect to the direction of light propagation, we have

$$\kappa = 0 ; \quad w = u. \quad \dots \dots \dots (74)$$

In other words, the velocity of light w in the material medium, moving with velocity v with respect to the æther, has the same velocity of propagation u as it would have were the material medium at rest. This is the Einstein condition, at least for air, whereas for media in which

$$n > 1$$

the resultant velocity w in the moving medium depends on v , according to the formula

$$w = u + \kappa v. \quad \dots \dots \dots (75)$$

It will be noted that only when we take in (75),

$$\kappa = 1,$$

making the slippage coefficient exactly unity, does the Newtonian compounding of velocities take place. Equations (50) above for moving dielectrics do not, therefore, follow the simple rule of Newtonian Mechanics.

To compare the Einstein addition formula of velocity vectors, namely,

$$\mathbf{w} = \frac{\mathbf{u} + \mathbf{v}}{1 + \frac{\mathbf{u}\mathbf{v}}{c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (76)$$

we have substantially that

$$\begin{aligned} \mathbf{w} &\equiv (\mathbf{u} + \mathbf{v}) \left(1 - \frac{\mathbf{u}\mathbf{v}}{c^2}\right) \\ &\equiv \mathbf{u} + \mathbf{v} - \frac{u^2\mathbf{v}}{c^2} - \frac{\mathbf{u}v^2}{c^2} \\ &\equiv \mathbf{u} \left(1 - \frac{u^2}{c^2}\right) + \mathbf{v} \left(1 + \frac{u^2}{v^2}\right). \quad . \quad . \quad . \quad (77) \end{aligned}$$

Since \mathbf{v} is the translational velocity of the dielectric, $\left(1 - \frac{v^2}{c^2}\right)$ is substantially equal to unity. Writing, however, κ for $1 - (u/c)^2$ in (77), we have, then, that

$$\mathbf{w} = \mathbf{u} + \kappa\mathbf{v}, \quad . \quad . \quad . \quad . \quad . \quad (75)$$

showing that under these circumstances there is accord between the Einstein relativity formula (76) and that of Classical Mechanics leading to (75).

Thus, writing according to (75) and (77) that

$$\kappa = 1 - \frac{u^2}{c^2}, \quad . \quad . \quad . \quad . \quad . \quad (78)$$

we need to have, according to the Fresnel formula

$$\kappa = 1 - \frac{1}{n^2}, \quad . \quad . \quad . \quad . \quad . \quad (79)$$

that

$$1 - \frac{u^2}{c^2} = \kappa = 1 - \frac{1}{n^2}. \quad . \quad . \quad . \quad . \quad (80)$$

This requires that the refractive index n be given by

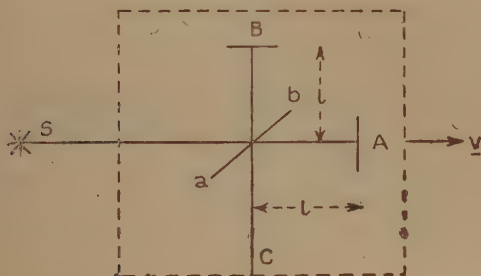
$$n = c/u. \quad . \quad . \quad . \quad . \quad (81)$$

PART III.

The Michelson-Morley Experiment in an Optically Dense Medium.

Light from a source S reaches a mirror *a*, *b*, and is partly reflected to B and partly transmitted to A. At the points

Fig. 3.



A and B the light is reflected back, meeting the eye at C. According to equation (72) we have

- \mathbf{v} = translational velocity of the medium,
- \mathbf{u} = velocity of light in the material medium when at rest relative to the æther,
- \mathbf{w} = resultant velocity of light in the material medium when in motion,

with the equation for the drag coefficient given by

$$\left. \begin{aligned} \mathbf{w} &= \kappa \mathbf{v} + \mathbf{u}; & \kappa &= \frac{w - u}{v}; \\ \kappa &= 1 - \frac{1}{n^2}; \end{aligned} \right\} \dots \dots (72)$$

In the latter n is the refractive index of the medium.

The light, in going from O to A, will have an actual velocity

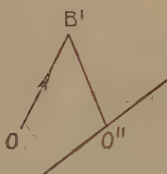
$$w_{OA} = \kappa \mathbf{v} + \mathbf{u},$$

and for the return journey it will be

$$\mathbf{w}_{AO} = -\kappa \mathbf{v} + \mathbf{u}.$$

However, the wave-length λ is similarly elongated, so that, so far as the number of wave-lengths set up is concerned,

Fig. 5.



the result is the same as if the light ray had only traversed the path

$$2OB = 2l.$$

Thus the number of wave-lengths really becomes

$$m' = \frac{2l}{\lambda}. \quad . \quad . \quad . \quad . \quad . \quad (86)$$

The difference Δ of the number of wave-lengths laid down by the light traversing the two types of paths is therefore

$$\begin{aligned} \Delta = (m - m') &= \frac{2l}{\lambda} \left[\frac{w}{u} \left(1 + \frac{\kappa^2 v^2}{u^2} \right) - 1 \right] \\ &= \frac{2l}{\lambda} \left[\left(\frac{w}{u} - 1 \right) + \left(\frac{w}{u} - 1 \right) \frac{\kappa^2 v^2}{u^2} + \frac{\kappa^2 v^2}{u^2} \right]. \end{aligned} \quad (87)$$

We note, however, that

$$\frac{w}{u} - 1 = \frac{w - u}{u} = \frac{w - u}{v} \cdot \frac{v}{u} = \kappa \frac{v}{u}, \quad . \quad . \quad (88)$$

whence (87) transforms to

$$\begin{aligned} \Delta &= \frac{2l}{\lambda} \left[\frac{\kappa v}{u} + \frac{\kappa^3 v^3}{u^3} + \frac{\kappa^2 v^2}{u^2} \right] \\ &= \frac{2l}{\lambda} \left[1 + \frac{\kappa v}{u} + \frac{\kappa^2 v^2}{u^2} \right] \kappa \cdot \frac{v}{u}. \quad . \quad . \quad . \quad (89) \end{aligned}$$

To a first approximation, therefore, with

$$\frac{v}{u} \ll 1,$$

$$\Delta \equiv \frac{2l}{\lambda} \cdot \frac{v}{u} \cdot \kappa \equiv \frac{2l}{\lambda} \cdot \frac{v}{u} \left(1 - \frac{1}{n^2} \right). \quad . \quad . \quad . \quad (90)$$

The formula usually employed for the Michelson-Morley experiment gives

$$\Delta_x = \frac{2l}{\lambda} \left(\frac{v}{c} \right)^2.$$

The above, (90), gives practically zero for air! The true effect with water or carbon disulphide should therefore be quite large, even for a span of $l=11$ cm. Turning the apparatus through 90° the value of Δ for the same l should be doubled, giving

$$\Delta_{90^\circ} = \frac{4l}{\lambda} \frac{v}{c} \left(\frac{c}{u} \cdot \kappa \right) = \frac{4l}{\lambda} \cdot \frac{v}{c} \cdot n\kappa. \quad \dots \quad (91)$$

The residual effect of Miller would thus seem to be accounted for.

August 1928.

LXX. *The Crystal Structure of Wurtzite.*

By M. LUTHER FULLER*.

ABSTRACT.

A METHOD of preparing wurtzite quite free from cubic zinc sulphide by heating cubic zinc sulphide with 10 per cent. of sodium chloride at 1100° C. is described.

The observed intensities on powder patterns are in good agreement with those calculated for space group $6c-4$ with $V=\frac{5}{8}$.

The unit-cell dimensions of wurtzite are found to be :

$a_0=3.811 \pm .004$ A, $c_0=6.234 \pm .006$ A, and $c/a=1.636$.

W. L. BRAGG⁽¹⁾, from a basal plane reflexion of a crystal of wurtzite, predicted the zinc oxide grouping to be the correct arrangement for wurtzite, the hexagonal form of zinc sulphide.

Aminoff⁽²⁾ and Ulrich and Zachariasen⁽³⁾, from powder patterns of wurtzite, confirmed the prediction of W. L. Bragg. The relative intensities of the diffraction maxima on the powder patterns obtained by these workers are not in

* Communicated by Prof. W. L. Bragg, F.R.S.

good agreement with those calculated from the assumed structure. This lack of agreement is considered by Aminoff, Ulrich and Zachariasen to be due to an admixture of crystals of sphalerite, the cubic form of zinc sulphide.

The tendency for wurtzite to revert partially to sphalerite, at room temperature, is well known. This change is easily brought about if the crystals are subjected to a mechanical strain such as grinding or crushing. It is difficult, however, to detect sphalerite in the presence of wurtzite, since all the strong diffraction lines of sphalerite are coincident with wurtzite lines. It seems reasonable to explain the discrepancies noted above, between the observed and calculated intensities of the lines, by assuming that the wurtzite reported in the literature^(2, 3) contained considerable sphalerite. Taking advantage of the published data on the properties of wurtzite, noted above, a small quantity of wurtzite was made and put into form suitable for crystal structure analysis in such a way as to produce the minimum sphalerite content. The diffraction patterns of this specimen gave good agreement between the observed and calculated intensities. It is the purpose of this paper to give the results in detail together with a precision measurement of the wurtzite lattice constants.

Experimental.

The specimen of wurtzite was prepared as follows: pure precipitated cubic zinc sulphide with ten per cent. of sodium chloride mixed with it, was heated at a temperature of 1100° C. for one hour. After the heating the sample was cooled to room temperature in about ten minutes. An atmosphere of hydrogen was maintained around the sample during the heating and the cooling. Without putting any mechanical strain on the crystals the sample was screened on a 325 mesh screen and the fine portion used for the X-ray specimen. When zinc sulphide is heated without sodium chloride, the product is not as free from cubic zinc sulphide as when sodium chloride is used. There is no evidence of sodium chloride crystals in the final product heated at 1100° C.

The General Electric X-ray diffraction apparatus described by Davey⁽⁴⁾ was used to obtain the patterns. Molybdenum K alpha radiation is used in this apparatus. Three films were made. In two of these exposures the

small glass specimen tube had the wurtzite in the one end of the tube and the calibrating substance, sodium chloride, in the other end ⁽⁵⁾. In each case the wurtzite and the sodium chloride were diluted with flour to reduce their opacity to about the same amount ⁽⁶⁾. In the third of these exposures the sodium chloride and wurtzite were mixed throughout the specimen tube ⁽⁷⁾.

The wurtzite crystals were too large to furnish sufficient orientations of the crystals to give continuous lines on the film. It was, therefore, necessary to slowly rotate the specimen tube during the exposure by means of a small clock the shaft of which was connected to an end of the specimen tube by a small rubber tube.

Calculation of the Results.

The interplanar spacings measured on the three films were corrected by means of a calibration made in terms of the sodium chloride spacings. The corrected spacings were in good agreement with each other and an average was taken from which the final calculations of the unit cell dimensions were made.

Thirteen interplanar spacings from 1.904 Å to 0.912 Å were used in the calculations. These spacings correspond to planes of Miller indices, 11.0, 10.3, 10.0(2), 11.2, 20.1, 10.1(2), 20.3, 21.0, 21.1, 10.0(3), 21.3, 11.0(2) and 11.6. Nine of these are the average of measurements on the three films and four are from two films, omitting the third because of the masking effect of the superimposed sodium chloride lines. The axial ratio was found graphically ⁽⁸⁾ to be between 1.634 and 1.640. A set of values of a_0 was calculated from the observed interplanar spacings and a given axial ratio for each value in this range. The results were plotted on probability paper ⁽⁹⁾, one curve for each value of the axial ratio. The curve plotted for axial ratio 0.636 is the closest to a true probability curve and gives $a_0=3.811$ Å from which $c_0=6.234$ Å. This method of calculating axial ratio is more completely described by the author in a previous paper ⁽¹⁰⁾.

The nature of the lines on the pattern was such that their position could be read with an accuracy of 0.1 per cent. over the range given above. The method of finding the axial ratio is more sensitive than 0.1 per cent. Hence the values of the unit cell dimensions are: $a_0=3.811 \pm 0.004$ Å and $c_0=6.234 \pm 0.006$ Å. The density calculated

from these data is 4.10 ± 0.01 . The density ⁽¹¹⁾ of the naturally occurring mineral wurtzite is given as 3.98. The density ⁽¹²⁾ of artificially prepared wurtzite is reported to be 4.087.

Table I. shows the average observed spacings of the three films and the observed intensities for two of the films. The observed intensities are estimated by eye and range from 10, very black, to 0+, extremely faint. The calculated intensities were calculated on the basis of the zinc oxide type of structure, space group $6c-4$ ($C^{46}V$) with $V = \frac{5}{8}$, according to the formula given by Wyckoff ⁽¹³⁾.

The empirical formulas used by various investigators for calculating the intensities of lines to be expected for a given crystal structure differ primarily in the value assigned to an exponent ⁽¹⁴⁾. Values for this exponent may be found in the literature varying from 2.00 to 3.00. It is better, instead of comparing actual values of observed and calculated intensities, to number the lines on the diffraction pattern in the order of their intensity, designating the most intense line as 1, the next most intense as 2, etc. ⁽¹⁵⁾. In this way the final result is relatively independent of the value chosen for the exponent in the formula. The difference between the numbers expressing the calculated and observed orders of intensity is then a measure of the agreement between theory and experiment. Of several attempted solutions, the one giving the smallest total error is the one to be taken as most probably correct.

Table II. gives, for comparison, the observed intensities of Aminoff and of Ulrich and Zachariasen. The order of the observed intensities is also given, as well as can be deduced from the published observed intensities. The total error in these two cases is much greater than that found in the evaluation of the patterns made by the present author.

The wurtzite lines corresponding to the planes 00.1(2), 11.0, 11.2, 00.1(4), 11.4, 10.0(3), 11.5, 00.1(6), 11.0(2), and 11.6 are coincident with lines on the pattern of sphalerite.

This investigation completely confirms the prediction of W. L. Bragg as to the structure of wurtzite, and indicates that the specimen used was quite free from cubic zinc sulphide.

It is a pleasure to thank Dr. W. P. Davey of Pennsylvania State College and Messrs. C. C. Nitchie and

TABLE I.

Planar Indices.	Average observed spacings.	Obs. Intensities, Film No. 1177.			Obs. Intensities, Film No. 1189.			Calc. Intensities.	
		Int.	Error.		Int.	Error.		Int.	Order.
			Order.			Order.			
10-0	3.29A	2	3	0	2	3	0	2.12	3
00-1(2)	3.11	0.6	7	1	1	5	3	1.29	8
10-1	2.91	1.9	4	0	1.9	4	0	1.77	4
10-2	2.27	0.5	9	1	0.5	10	0	0.91	10
11-0	1.904	2.5	2	0	2.3	2	0	2.31	2
10-3	1.759	2.5	1	0	2.5	1	0	2.48	1
10-0(2)	1.651	0.1	19	2	0.1	20	3	0.41	17
11-2	1.628	0.8	5	0	0.9	6	1	1.75	5
20-1	1.593	0.2	12	3	0.1	16	1	0.43	15
10-1(2)	1.458	0.1	17	2	0.1	18	1	0.32	19
20-3	1.292	0.5	8	1	0.6	8	1	1.20	9
21-0	1.249	0.1	14	3	0.1	13	2	0.90	11
21-1	1.224	0.1	16	2	0.1	15	1	0.46	14
10-5 }	1.166	0.3	10	3	0.5	9	2	1.03	7
21-2 }								0.40	
10-0(3) }	1.099	0.2	11	2	0.2	11	2	0.64	13
21-3 }	1.068	0.6	6	0	0.7	7	1	1.54	6
11-5 }	1.038	0.1	18	2	0.1	19	1	0.00	20
00-1(6) }								0.10	
20-5 }	0.995	0.1	15	3	0.1	14	2	0.75	12
10-6 }								0.09	
11-0(2) }	0.955	0.1	20	2	0.1	17	1	0.40	18
11-6 }	0.912	0.2	13	3	0.2	12	4	0.42	16
		Total error ... 30			Total error ... 26				

TABLE II.
Comparison of Observed Intensities.

Planar Indices.	Film No. 1177*.		Film No. 1189*.		Aminoff.		Ulrich and Zachariasen.		Calc. Intensities.		
	Int.	Order. Error.	Int.	Order. Error.	Int.	Order. Error.	Int.	Order. Error.	Int.	Order.	
10-0	2.0	3	2.0	3	2	6	2	10	2.12	3	
00-1(2)	0.6	7	1.0	5	3	4	4	3	1.29	8	
10-1	1.9	4	1.9	4	1	8	2	11	1.77	4	
11-0	2.5	2	2.3	2	4	1	5	1	2.31	2	
10-3	2.5	1	2.5	1	1	7	3	7	2.48	1	
11-2	0.8	5	0.9	6	4	2	4.5	2	1.75	5	
20-3	0.5	8	0.6	8	1	13	2	12	1.20	9	
21-0	0.1	11	0.1	11	1	11	2.5	9	0.90	10	
10-5	0.3	9	0.5	9	1	10	3	8	1.03	7	
21-2	0.2	10	0.2	10	3	5	4	4	0.40	8	
10-0(3)	0.6	6	0.7	7	1	9	3.5	6	0.64	12	
21-3	0.1	13	0.1	13	4	3	4	5	1.54	0	
11-5	0.1	12	0.1	12	1	12	2	13	0.00	13	
00-1(6)	0.1	12	0.1	12	1	12	2	13	0.10	11	
20-5	0.1	12	0.1	12	1	12	2	13	0.75	11	
10-6	0.1	12	0.1	12	1	12	2	13	0.09	11	
Total error ...		8	Total error ...		12	Total error ...		50	Total error ...		52

* These data differ from those of Table I, in that only those lines are included which are given in the published data of Aminoff and Ulrich and Zachariasen. This makes possible a direct comparison of the data.

H. M. Cyr of this laboratory for their helpful advice during the course of this investigation.

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LXXI. *Electron Scattering and High Frequency Radiation.*
By J. A. C. TEEGAN, M.Sc., Lecturer in Physics,
University College, Rangoon.*

1. M. DE BROGLIE has introduced a new system of mechanics according to which a moving particle behaves as a group of waves of velocity and frequency governed by the mass and speed of the particle. If m_0 is the mass, and v the velocity, the frequency is given by

$$\nu = \frac{m_0 cv}{h \sqrt{1 - \frac{v^2}{c^2}}}. \quad \dots \dots (1)$$

The waves are considered as possessing no energy, being simply geometrical phase waves, so that the fact of their velocity $V \left(= \frac{c}{v} \right)$, being greater than the velocity of light is not impossible.

Considering such waves associated with an electron, their frequency will depend on the velocity v , and for a value of the velocity equal to $\frac{c}{10}$ will be about the same as that of moderately hard gamma-rays.

* Communicated by Prof. W. L. Bragg, F.R.S.

2. G. P. Thomson (Proc. Roy. Soc. A, clxii. p. 600 (1928)) has examined the diffraction of homogeneous beams of cathode rays in passing through thin metal films. These metal films consist of a number of minute crystals arranged at random, and the photographic diffraction patterns obtained in all cases are identical with those obtained in the Hull-Debye-Scherrer apparatus, employed for the diffraction of X-rays. Calculation from the diffraction patterns is in excellent agreement with the "De Broglie" conception of electron waves.

3. If the wave hypothesis of the electron be extended to the absorption of high speed electrons in matter, some interesting conclusions regarding the nature of the so-called "cosmic-rays" may be derived. The view that these penetrating radiations consist of short "gamma-rays" has been prevalent because their large penetrating power is associated with radiation of the gamma-ray type. Millikan, from an analysis of his "depth-ionization" curve, singled out three homogenous groups of penetrating cosmic radiation, with absorption coefficients in matter equal to $\cdot 35$, $\cdot 08$, and $\cdot 04$ metre⁻¹. Assuming the radiation of the γ -ray type, the wave-lengths of these radiations were calculated from the absorption formula of Dirac* :—

$$S = \frac{2\pi N e^4}{m^2 c^4} \frac{1+\alpha}{\alpha^2} \left\{ \frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha} \log(1+2\alpha) \right\}$$

where $\alpha = \frac{h\nu}{mc^2} \dots \dots \dots (2)$

The wave-lengths came out to be ($\cdot 35 \times 10^{-11}$ cm., $\cdot 117 \times 10^{-11}$ cm., and $\cdot 059 \times 10^{-11}$ cm.), which were in excellent agreement with the attractive supposition that these penetrating radiations have their origin in the formation of the most abundant atoms.

Subsequently the Dirac formula has been modified by Klein and Nishina ('Nature,' September 15th, 1928) as follows :—

$$S = \frac{2\pi N e^4}{m^2 c^4} \left\{ \frac{1+\alpha}{\alpha^2} \left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha} \log(1+2\alpha) \right] + \frac{1}{2\alpha} \log(1+2\alpha) - \frac{1+3\alpha}{(1+2\alpha)^2} \right\} \dots \dots (3)$$

The introduction of the last term in this formula leads

* Dirac, Proc. Roy. Soc. A, cxi. p. 423 (1926).

to a deviation from the Dirac formula of the order $\left(\frac{h\nu}{mc^2}\right)$, and the wave-lengths of the cosmic-rays come out lower when calculated on the Klein and Nishina theory. Thus the most penetrating cosmic-rays observed by Millikan have a wave-length equal to $\cdot 013 \times 10^{-11}$ cm., corresponding to a quantum of energy of 940 million volts. The origin of this radiation is traced to the annihilation of matter by the coalescence of protons and electrons, which Eddington assumes is taking place in the interior of the hot stars.

4. Denoting the frequency of a radiation by ν_1 ,

$$h\nu_1 = m_0 c^2 \left(\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} - 1 \right) \dots \dots \dots (4)$$

where v is the velocity of an electron whose energy corresponds to that of the radiation.

Such an electron will be accompanied by "De Broglie" waves of frequency ν_2 given by :—

$$\nu_2 = \frac{m_0 v c}{h \sqrt{1 - \frac{v^2}{c^2}}} \dots \dots \dots (5)$$

Obviously, when v is approximately equal to c , the two frequencies ν_1 and ν_2 are almost identical, so that the frequency of a very penetrating gamma radiation will differ only very slightly from that of the "De Broglie" waves of an electron, whose energy corresponds to that of the gamma-ray quantum.

5. Assuming that high speed electrons are scattered by matter in the same manner as gamma-rays, of the same frequency as that of their accompanying electron waves, the Klein-Nishina formula may be applied to their absorption

by substituting for the mass of the gamma-ray quantum $\frac{h\nu}{c^2}$ the electronic mass

$$(m) = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}.$$

The "mass" of a very high frequency gamma-ray quantum

$\frac{h\nu}{c^2}$ is, however, almost identical with that of an electron (m) of corresponding energy. Actually

$$\frac{h\nu}{c^2} = \left(1 - \sqrt{1 - \frac{v^2}{c^2}}\right) m, \quad (6)$$

which for values of $\frac{v}{c}$ close to unity reduces approximately

$$\text{to } \frac{h\nu}{c^2} = m.$$

6. A very slight difference in the absorption coefficients will therefore result if m is substituted for $\frac{h\nu}{c^2}$ in the Klein and Nishina expression, and we have the interesting result that the absorption coefficient of electrons (or electron waves) of very high velocity should differ only very slightly from that of a gamma radiation of the same energy. Thus electrons corresponding to 940 million volts might be expected to behave in their absorption by matter in a manner almost identical with that of a gamma radiation of corresponding wave-length (0.13×10^{-11} cm.); and it would not appear possible to predict, from a study of its absorption, whether the most penetrating of the cosmic radiations is of a corpuscular or gamma-ray nature.

LXXII. *Photoelectric Thresholds of the Alkali Metals.* By N. R. CAMPBELL. (Communication from the Research Laboratories of the General Electric Company, Limited, Wembley.) *

H. E. IVES and A. R. OLPIN † have recently described experiments indicating that the photoelectric thresholds of thin films of the alkali metals are identical with the resonance potentials of their neutral atoms; on this identity they have founded a tentative theory of the photoelectric effect. This theory is not easily reconciled with Sommerfeld's theory

* Communicated by the Director.

† H. E. Ives and A. R. Olpin, *Phys. Rev.* xxxiv. p. 117 (1929).

of the metallic state, which has been applied to the photoelectric effect with some success by Fowler *. It may be well, therefore, to point out that their conclusions, though doubtless perfectly valid for the instances that they examined, may not have the generality that they are inclined to attribute to them.

It seems to be a consequence of their theory that the threshold of a thin film of the alkali metals should be independent of the surface upon which it is deposited. This is proved by their experiments, when this surface is gas-free platinum or silver; it may possibly be true, as they suggest, whenever the surface is gas-free. Some experiments conducted in these laboratories suggest that the threshold is displaced towards longer wave-length when other metals, and in particular gold, are used as the support for the thin film; but there is some uncertainty whether the gold surfaces that were employed were truly gas-free.

However, it is certain that, if the support for the thin film is not a gas-free metal surface, but a metal surface deliberately oxidized, the threshold is not identical with the resonance potential of the alkali metal. Thus thin films of potassium deposited on oxidized surfaces of copper † have thresholds that certainly lie on the long wave-length side of 0.85μ , while thin films of caesium deposited on oxidized silver ‡ have thresholds that lie on the long wave-length side of 1μ . The resonance potentials of potassium and caesium are given by Ives and Olpin as 0.79μ and 0.89μ .

It should be observed that it is much easier to establish experimentally that the threshold lies on the long wave-length side of some limit than that it lies on the short wave-length side. For since the emission falls towards the threshold from the short wave-length side, a failure to find emission on the short wave-length side may indicate merely that the method of detecting a photoelectric current was not sufficiently sensitive. If, however, a photoelectric current is detected on the long wave-length side of the limit, there can be no doubt that the threshold lies on that side.

* R. H. Fowler, *Proc. Roy. Soc. A*, cxviii. p. 229 (1928).

† N. R. Campbell, *Phil. Mag.* vii. p. 633 (1928).

‡ L. R. Koller, *Gen. Elec. Rev.* xxxi. p. 476 (1928).

LXXIII. *Freezing-point Measurements in Very Dilute Solutions of Strong Electrolytes in Cyclohexanol.* By Professor E. SCHREINER *, Ph.D., O.E. FRIVOLD, M.Sc., Ph.D., and F. ENDER, M.A.†

Introduction.

IN an earlier paper‡ we have given some results of freezing-point measurements in very dilute solutions of uni-univalent salts in a solvent with a small dielectric constant, viz., cyclohexanol $D=15.0$.

It appears plainly from these measurements that the electric properties of the solvent have a great influence on the osmotic behaviour of a solution. The results obtained from these freezing-point measurements also indicate good agreement with the Debye-Hückel theory, according to which the relative deviations of the freezing-point depression from the values to be found in an ideal solution are inversely proportional to $D^{3/2}$.

This is in many respects quite remarkable, as, according to the theory, one may expect deviations in solvents with a small dielectric constant. For in Debye-Hückel's theory certain approximations have been made by deduction of the laws found, the influence of which will be the stronger the less the dielectric constant, viz., the greater the inter-ionic forces. It seemed to us of importance, therefore, to extend the freezing-point measurements also to uni-bivalent and uni-trivalent salts in the same solvent, as the influence of the greater charges must be expected to be stronger than those of uni-univalent salts.

For the same reason measurements were made with mixtures of one uni-univalent and one uni-trivalent salt.

Besides this solvent having a dielectric constant of the right magnitude, cyclohexanol is also adapted for this purpose by having a great freezing-point constant—about 20 times that of water. It was therefore possible to make freezing-point measurements with a Beckmann thermometer divided in $1/1000$ degree centigrade. The pure solvent has a freezing-point at about 24°C. , which makes it suitable for freezing-point measurements. The only disadvantage is that

* We regret to record that Professor E. Schreiner, with whom we have co-operated in the preparation of this paper, passed away shortly before its completion. His passing leaves us with a deep sense of personal bereavement.—O. E. F., F. E.

† Communicated by Prof. Sem Sæland.

‡ *Zeits. f. phys. Chem.* cxxiv. p. 1 (1926).

670 Prof. Schreiner, Dr. Frivold, and Mr. Ender on the cyclohexanol is very hygroscopic. It was therefore necessary to carry out the measurements in a closed apparatus.

Apparatus.

The same apparatus previously described for freezing-point measurements of uni-univalent salts was used for these measurements also, viz., a modified Beckmann apparatus. The stirrer consisted of pure silver (*loc. cit.*). The Beckmann apparatus was closed in order to keep out the humidity of the air. The stirrer was therefore equipped with a mercury fitting (see Ostwald-Luther, 'Physiko-Chemische Messungen,' 3rd ed., p. 276).

Precautions against Errors.

In the former paper reference has been made to many errors which may have an influence upon the measurements, especially on account of the hygroscopy of the solvent and errors by the Beckmann thermometer. Special care was taken in order to calibrate the thermometers used.

Solvent and Salts.

Cyclohexanol (from Poulenc Frères, Paris) was twice distilled in a vacuum at about 2–3 mm. mercury pressure. The first fraction contained small quantities of water. The freezing-point of the main fraction in the second distillation varied between 23.3 and 23.9 degrees centigrade in the different cases, and could not be raised appreciably more. This fraction was used for the measurements, and the mean value, 23.6 C., was used for the calculation of the results obtained.

The following three salts were employed in the measurements:—

LiCl, from Poulenc Frères, was dissolved in alcohol (absolute), and to the solution was added Li_2CO_3 . After being filtered, the solution was evaporated on a water-bath and then heated in a platinum vessel until the salt was thoroughly melted. After cooling, the same procedure was repeated. The pulverized salt was at last heated about 12 hours in a drying-oven, at about 160°, until the weight was constant.

Pure uranyl acetate, from Kahlbaum, was used. The salt was freed from water of crystallization and dried until it showed constant weight.

$\text{La}(\text{NO}_3)_3$, from Merck, was heated about 12 hours at 120°. It was then heated for about the same time at the same

temperature in vacuum, and lastly about 24 hours at 150° to 155° . After being pulverized it was heated about 12 hours at 150° until the weight was constant.

Results of Measurements.

In the following pages the freezing-point depression of an ideal solution is indicated by Δ . This can be calculated when the freezing-point constant is known. $\Delta = \nu k \gamma$, where ν is the number of ions in a molecule, k is the freezing-point constant, and γ is the concentration of the solution in mols per litre.

If the freezing-point depression measured is indicated by $\bar{\Delta}$, then

$$\frac{\bar{\Delta} - \Delta}{\Delta} = 1 - \frac{\Delta}{\bar{\Delta}} = 1 - g$$

gives us the relative deviation of the measured freezing-point from the classical value. g is the osmotic coefficient according to Bjerrum, and $1 - g$ therefore the deviation of the osmotic coefficient from its limiting value. The magnitude $1 - g$, in the tables as well as in the figures, has been given in its dependence of the square root of the ionic concentration.

The freezing-point constant was found before :

$$k = 38.2 \pm 0.1.$$

As the salts used are very hygroscopic, it was necessary to work with a standard solution of the salt in cyclohexanol. From this it was added to the Beckmann apparatus, which originally contained the pure solvent.

The experiments with mixtures containing LiCl and $\text{La}(\text{NO}_3)_3$ were performed in the following way. In the bottle where the standard solution was made, weighed quantities of the two salts were dissolved in cyclohexanol in such a way that the ratio p between the two molalities δ (of $\text{La}(\text{NO}_3)_3$) and γ (of LiCl) was very near $\frac{1}{3}$, $\frac{1}{2}$, and 1 in the different cases.

From such a standard solution a portion was added to the Beckmann apparatus by aid of a pipette, and freezing-point measurements were made (*loc. cit.*)...

If we use the following notations, $p = \frac{\delta}{\gamma}$; ϕ and ν = number of ions in a molecule of $\text{La}(\text{NO}_3)_3$ and LiCl , we get

$$\bar{\Delta} = k(\nu\gamma + \phi\delta) = k(\nu + p\phi)\gamma.$$

The results of the measurements will be found in the following tables.

In Tables I., II., III., IV., and V., under γ will be found the concentration expressed in mole salt in 1000 c.c. solution (in the case of the mixtures γ indicates the concentration of LiCl); in the second column will be found the square root of the ionic concentration; $\bar{\Delta}$ is the calculated freezing-point depression for an ideal solution; Δ is the depression actually observed; $1-g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}$; $(1-g)_{\text{corr.}}$ are the values of $1-g$ corrected for the humidity (*loc. cit.*).

TABLE I.— $\text{La}(\text{NO}_3)_3$.

$$1-g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}; \bar{\Delta} = k.4\gamma; k = 38.22.$$

γ .	$\sqrt{4\gamma}$.	$\bar{\Delta}$.	Δ .	$1-g$.
0.000223	0.030	0.034	0.012	0.64
0.000500	0.045	0.076	0.027	0.65
0.000934	0.061	0.143	0.044	0.69
0.002919	0.108	0.446	0.086	0.81
0.004933	0.141	0.754	0.143	0.81
0.008037	0.179	1.229	0.269	0.78
0.01105	0.210	1.689	0.387	0.77
0.01279	0.226	1.956	0.450	0.77

Second Series.

0.000618	0.050	0.094	0.034	0.64
0.000808	0.057	0.124	0.052	0.58
0.001310	0.072	0.200	0.058	0.71
0.002462	0.099	0.376	0.103	0.73
0.00	0.128	0.629	0.183	0.71
0.006217	0.158	0.951	0.257	0.73
0.008109	0.180	1.240	0.334	0.73
0.01131	0.213	1.728	1.448	0.74
0.01215	0.221	1.858	0.482	0.74

TABLE II.— $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$.

$$1 - g = \frac{\bar{\Delta} - \Delta}{\Delta} ; \bar{\Delta} = k \cdot 3\gamma ; k = 38.22.$$

γ .	$\sqrt{3\gamma}$.	$\bar{\Delta}$.	Δ .	$1 - g$.	
				Measured.	Corrected.
0.00118	0.060	0.135	0.081	0.40	0.39
0.002236	0.082	0.2564	0.1206	0.530	0.516
0.003828	0.107	0.4389	0.2103	0.521	0.507
0.005913	0.140	0.6780	0.3134	0.538	0.524

Second Series *.

0.000589	0.042	0.067	0.053	0.22	
0.001233	0.061	0.141	0.072	0.49	
0.002343	0.084	0.2686	0.1286	0.521	
0.004029	0.110	0.4620	0.2179	0.528	
0.005593	0.130	0.6413	0.3056	0.524	
0.007123	0.146	0.8167	0.3634	0.556	

Third Series.

0.001656	0.071	0.190	0.086	0.55	0.51
0.002612	0.089	0.300	0.1340	0.553	0.517
0.004690	0.119	0.5377	0.2221	0.587	0.552
0.006620	0.141	0.7590	0.3493	0.540	0.504

Fourth Series.

0.001436	0.066	0.165	0.084	0.49	0.48
0.002630	0.089	0.3015	0.1504	0.501	0.491
0.005137	0.124	0.5891	0.2487	0.578	0.568
0.006545	0.140	0.7504	0.3194	0.574	0.565
0.007427	0.149	0.8516	0.3795	0.554	0.544

* For this and other cases the correction for the humidity was without influence.

TABLE III.—LiCl + La(NO₃)₃.

$$1-g = \frac{\bar{\Delta}-\Delta}{\Delta}; \quad \bar{\Delta} = k(\nu+p\phi)\gamma; \quad k=38.22; \quad \nu=2; \quad \phi=4; \\ p=0.126 \approx \frac{1}{8}.$$

γ .	$\sqrt{(\nu+p\phi)\gamma}$.	$\bar{\Delta}$.	Δ .	$1-g$.	
				Measured.	Corrected.
0.000695	0.042	0.067	0.049	0.26	0.26
0.001731	0.066	0.1657	0.1077	0.350	0.345
0.003146	0.089	0.3008	0.1828	0.392	0.387
0.006025	0.123	0.5760	0.3399	0.410	0.405
0.0109	0.165	1.043	0.5650	0.458	0.453
0.01365	0.185	1.306	0.7071	0.458	0.453

Second Series. $p=0.125$.

0.001840	0.068	0.1757	0.1127	0.359	
0.003466	0.093	0.3311	0.1953	0.410	
0.006395	0.126	0.6108	0.3540	0.420	
0.008790	0.148	0.8395	0.4357	0.481	
0.01272	0.178	1.2149	0.6306	0.481	
0.02682	0.259	2.562	1.295	0.495	
0.04720	0.343	4.508	2.209	0.510	
0.06570	0.406	6.275	3.043	0.515	
0.07641	0.437	7.298	3.494	0.521	

TABLE IV.—LiCl + La(NO₃)₃.

$$1-g = \frac{\bar{\Delta}-\Delta}{\Delta}; \quad \bar{\Delta} = k(\nu+p\phi)\gamma; \quad k=38.22; \quad \nu=2; \quad \phi=4; \\ p=0.505.$$

γ .	$\sqrt{(\nu+p\phi)\gamma}$.	$\bar{\Delta}$.	Δ .	$1-g$.	
				Measured.	Corrected.
0.000590	0.049	0.0907	0.0459	0.49	
0.001800	0.085	0.2766	0.1279	0.538	
0.002882	0.108	0.4429	0.1835	0.586	
0.004418	0.133	0.6791	0.2813	0.586	
0.007571	0.175	1.1637	0.4709	0.595	

TABLE IV.—LiCl + La(NO₃)₃ (cont.).

$$1-g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}; \bar{\Delta} = k(\nu + p\phi)\gamma; k = 38.22; \nu = 2; \phi = 4; \\ p = 0.505.$$

Second Series. $p = 0.5005$.

γ .	$\sqrt{(\nu + p\phi)\gamma}$.	$\bar{\Delta}$.	Δ .	$1-g$.	
				Measured.	Corrected.
0.000582	0.048	0.0891	0.0476	0.47	0.45
0.001193	0.069	0.1828	0.0897	0.509	0.493
0.001788	0.085	0.2740	0.1346	0.508	0.492
0.002884	0.0108	0.4415	0.1907	0.569	0.554
0.003870	0.0124	0.5935	0.2580	0.566	0.551
0.00666	0.0164	1.020	0.4290	0.580	0.565

Third Series. $p = 0.504$.

0.000623	0.050	0.0956	0.0472	0.51	0.50
0.001011	0.064	0.1553	0.0799	0.486	0.481
0.001680	0.082	0.2579	0.1183	0.541	0.536
0.003518	0.119	0.5401	0.2382	0.559	0.553
0.006229	0.158	0.9563	0.4067	0.575	0.569
0.008151	0.181	1.2513	0.5157	0.588	0.583

TABLE V.—LiCl + La(NO₃)₃.

$$1-g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}; \bar{\Delta} = k(\nu + p\phi)\gamma; k = 38.22; \nu = 2; \phi = 4. \\ p = 1.01.$$

γ .	$\sqrt{(\nu + p\phi)\gamma}$.	$\bar{\Delta}$.	Δ .	$1-g$.
0.0002689	0.040	0.0621	0.0315	0.49
0.0008628	0.072	0.1992	0.0828	0.58
0.001357	0.091	0.3132	0.1362	0.565
0.003197	0.139	0.7381	0.2749	0.628
0.006012	0.191	1.3878	0.4900	0.647
0.006957	0.205	1.6060	0.5394	0.664

Second Series. $p = 1.01$.

0.001082	0.081	0.2498	0.0905	0.64
0.001837	0.105	0.4241	0.1585	0.626
0.005398	0.181	1.2461	0.4215	0.662

Testing of the Debye-Hückel Osmotic Theory.

According to Debye-Hückel's theory, the relative deviation of the freezing-point depression from the classical value is

$$1-g = \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2 N}{1000DkT}} \cdot \omega \sqrt{\nu\gamma} \cdot \sigma(\kappa a), \quad (1)$$

where

$$\omega = \left(\sum \frac{\nu_i z_i^2}{\nu} \right)^{3/2},$$

$$\epsilon = 4.77 \cdot 10^{-10} \text{ e.s.u.},$$

$$k \text{ (Boltzmann's constant)} = 1.37 \cdot 10^{-16} \text{ erg.},$$

$$N = 6.06 \cdot 10^{23},$$

$$D = \text{Dielectric constant},$$

$$T = \text{Temperature abs.},$$

$$\gamma = \text{Concentration in mole/litre.}$$

The salt molecules are split in $\nu_1, \nu_2, \dots \nu_i$ ions of the kind 1, 2, $\dots i$, $\nu = \sum \nu_i$. The valencies of the different ions are indicated by $z_1, z_2, \dots z_i$. $\sigma(xa)$ is a function whose value is less than one, and is dependent on the ratio between the ionic diameter a , and the dimension of the ionic atmosphere $\frac{1}{\kappa}$ gives us a measure for this atmosphere. By infinite dilution $\sigma(\kappa a) = 1$.

For a solution of infinite dilution the function tends towards 1, viz., in such solutions the influence of the dimensions of the ions disappears in comparison with the influence of the ionic atmosphere. In this case it will be seen from formula (1) that $1-g$ is proportional to the square root of the ionic concentration, viz., if we plot $1-g$ in relation to $\sqrt{\nu\gamma}$, it must be expected that curves through the points experimentally found and point of origin in small concentrations will coincide with the tangents theoretically calculated. The slopes of these tangents are, according to the theory, determined by the known quantities ϵ, k, T, N , of the dielectric constant D , and the valency factor ω .

Mixtures of Electrolytes.

For mixtures of electrolytes we get an expression for $1-g$ quite similar to formula (1).

We dissolve γ mole per litre of a salt (LiCl) whose molecules are split in $\nu_1, \nu_2, \dots \nu_i$ ions of the kind 1, 2, 3, $\dots i$. The valencies of the ions we indicate by $z_1, z_2, \dots z_i$, $\sum \nu_i = \nu$.

We dissolve also δ mole per litre of another salt, $\text{La}(\text{NO}_3)_3$, whose molecules are split in $\phi_1, \phi_2, \dots \phi_i$ ions of the kind $1, 2, 3, \dots i$. The valencies of the ions we indicate by $x_1, x_2, \dots x_i, \Sigma \phi_i = \phi$.

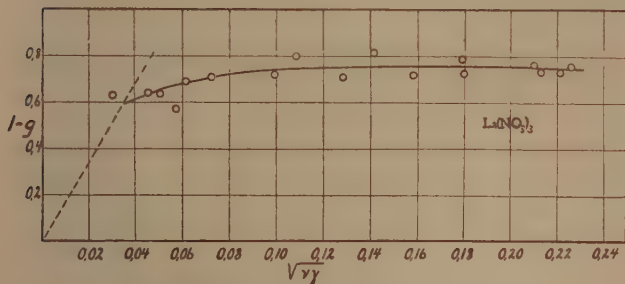
For this mixture of two electrolytes we have, denoting $\frac{\delta}{\gamma}$ by p ,

$$1-g = \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2 N}{1000 \cdot DkT}} \omega \sqrt{(\nu + p\phi)\gamma},$$

$$\omega = \left(\frac{\gamma \Sigma \nu_i z_i^2 + \delta \Sigma \phi_i x_i^2}{\nu \gamma + \phi \delta} \right)^{3/2} = \left(\frac{\Sigma \nu_i z_i^2 + p \Sigma \phi_i x_i^2}{\nu + p\phi} \right)^{3/2}.$$

Measurements were made with solutions where p is very nearly equal to $\frac{1}{8}$, $\frac{1}{2}$, and 1. For these values of p it will be found that $\omega_{1/8} = 5.47$, $\omega_{1/2} = 9.34$, and $\omega_1 = 11.77$.

Fig. 1.



Discussion of the Results obtained.

In figs. 1, 2, 3, and 4 are plotted the relative deviations of the freezing-point depression from the classical values in relation to the square root of the ionic concentration. The results obtained for LiCl , $\text{La}(\text{NO}_3)_3$ for mixtures of these two salts and for uranyl acetate will be found. In the same figures the theoretically calculated tangents are plotted.

It will be seen from the graphical representation that it will be necessary to perform sufficiently accurate freezing-point measurements at considerable lower concentrations for $\text{La}(\text{NO}_3)_3$ than for LiCl in order to be able to test the limiting law. On account of this it has been impossible by these experiments to test the limiting law to the same extent as has been the case with the uni-univalent salts.

The graphical representations show, however, especially as regards the mixtures, that the curves experimentally found do not coincide with the tangents theoretically calculated, as was the case with the uni-univalent salts, in very small concentrations. The results obtained by the uni-bivalent uranyl acetate do not seem to conflict with the theory.

Fig. 2.

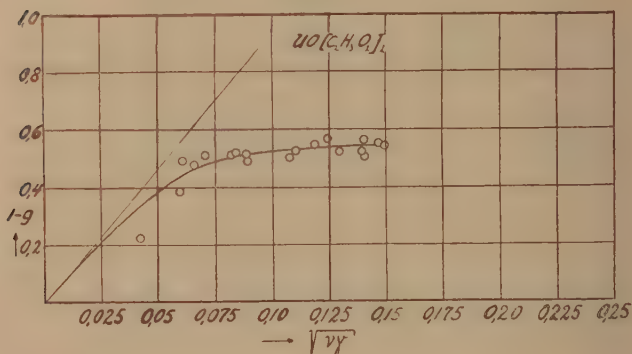
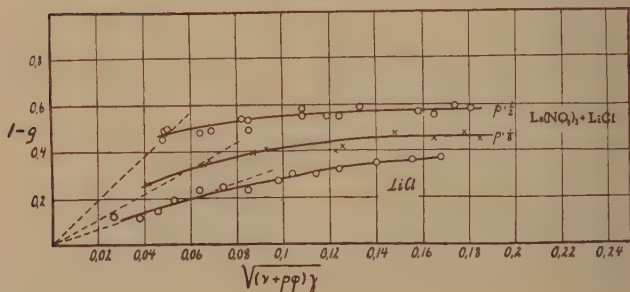


Fig. 3.



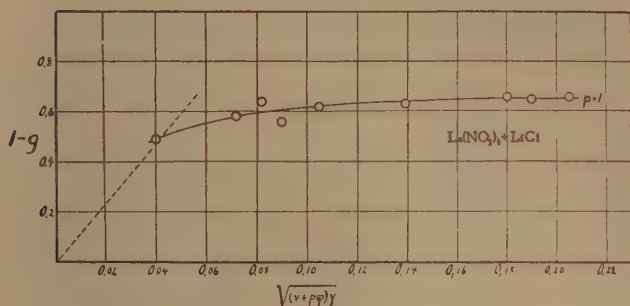
Deviations from the theory of the same nature as found by the mixtures have also been found by Brønsted and Petterson, and later on by La Mer and Mason* in aqueous solutions by solubility measurements. This is the case at small concentrations, when the solution contains saturating salts with high-valence cations in the presence of solvent salts with high-valence anions.

* Journ. Amer. Chem. Soc. xlix. p. 410 (1927).

At the same time it appears that the mean ionic diameter calculated according to theory varies in many cases to a great extent with the concentration—the calculated values for the ionic diameters are improbably small or negative. These discrepancies with the theory have caused Müller*, Gronwall, La Mer and Sandved† to examine the influence of the approximation made in the Debye-Hückel theory introduced by the calculation of the distribution of the potential round a particular ion.

These investigators have solved this problem with a greater approximation than Debye and Hückel, and also found that more of the deviations mentioned above of the aqueous solutions will disappear under these circumstances.

Fig. 4.



The improved theory shows that the discrepancies from the Debye-Hückel's theory will be greater the less the ionic diameter, and the greater the valencies of the ions. According to the improved theory for small ionic diameters, the curves, indicating the connexion between $1-g$ and $\sqrt{v\gamma}$, will cut the theoretically-calculated tangents in the same way as found by us experimentally with the mixtures (figs. 3 and 4), and by infinite dilution will join the theoretical tangent, according to Debye-Hückel's theory.

Otherwise it is to be observed that the result found by Gronwall, La Mer and Sandved by the calculation of the activity coefficient only can be applied to salts of the symmetrical type, as KCl and CuSO_4 ; on the contrary, not on asymmetrical salts, like $\text{La}(\text{NO}_3)_3$, or mixtures of two salts.

* Müller, *Phys. Zeits.* 1927, p. 324; 1928, p. 78.

† T. H. Gronwall, La Mer and K. Sandved, *Phys. Zeits.* Bd. xxix. p. 358 (1928).

Nor are there measurements accurate enough for non-aqueous solutions which make a comparison possible between the improved theory and the experiments. But so much can be said—that the greater the valencies of the dissolved ions are, and the less the dielectric constant of the solvent, the greater the deviations that can be expected from the original Debye-Hückel theory.

Owing to lack of room the above measurements were carried out in the Pharmacological Institute, thanks to the courtesy of the professor, Dr. E. Poulsson.

We also wish to express our thanks to the directors of the "A/S Norsk Varekrigsforsikrings Fond," who have granted the funds necessary to carry out this work.

Physical Department,
University, Oslo,
March 1929.

LXXIV. *Double-Valued Characteristic of a Direct Current Feed-Back Amplifier.* By PRESTON B. CARWILE, *Ph.D.*, and FREDERIC A. SCOTT, *M.S.*, *Lehigh University, U.S.A.* *

A MODIFIED Hartley † direct current feed-back amplifying circuit with connexions as shown in fig. 1, exhibits an anomalous static characteristic under certain feed-back conditions. It is the purpose of the present paper to describe and explain this effect.

Let m be the voltage amplification of the two ‡ tube circuit due to thermionic action alone, M the total voltage amplification due to thermionic and feed-back action combined, R the external resistance in the plate circuit of tube 2, r that portion of R between the filament and the feed-back tap T , I_p the current through R , E_g' the grid potential of tube 1, and E_g the portion of E_g' furnished externally (as by potentiometer P), exclusive of the potential due to feed-back action.

* Communicated by the Authors.

† R. V. L. Hartley, 'U.S. Letters Patent,' No. 1, 218, 650. See also van der Bijl, 'The Thermionic Vacuum Tube and its Applications,' p. 257.

‡ It is necessary to use at least two tubes in a direct current feed-back amplifier in order that the feed-back and input potentials may be in phase.

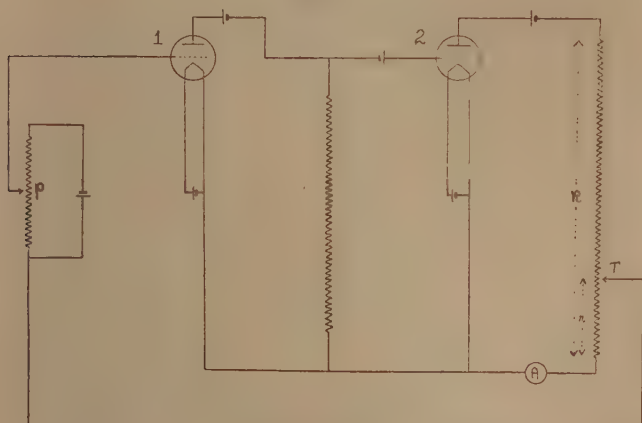
Assuming that there is no grid current through tube 1 it can easily be shown * that

$$M = m \left[1 + \left(\frac{r}{R} m \right) + \left(\frac{r}{R} m \right)^2 + \left(\frac{r}{R} m \right)^3 \dots \right]$$

$$= \frac{m}{1 - \frac{r}{R} m}, \quad \dots \dots \dots (1)$$

provided $\frac{r}{R} m < 1$. Thus the total amplification M approaches infinity as $\frac{r}{R} m$ approaches unity.

Fig. 1.



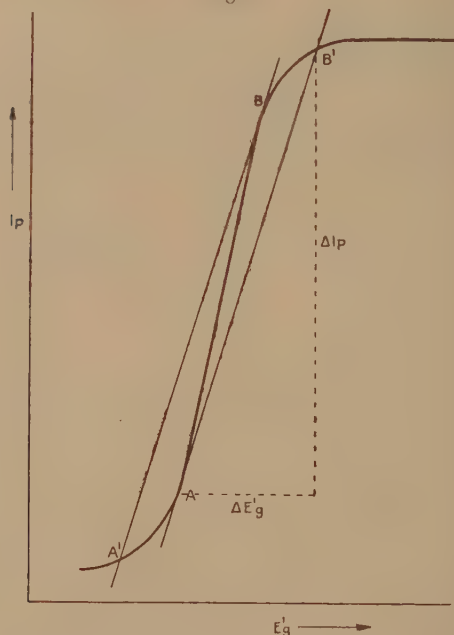
First let us consider a "base" characteristic, *i. e.* one obtained by pure thermionic action with no feed-back ($r = 0$). If we plot I_p as ordinates and E_g' as abscissæ (plotting negative values, however, towards the right) we shall have a curve of the form shown in fig. 2. It is readily seen that the slope of this curve is proportional to the voltage amplification. Hence, in terms of arbitrary units we may say that the slope is the amplification m .

This base characteristic still applies, even with feed-back action taking place, since E_g' is the *actual* grid potential whether obtained from an external source or from the feed-back tap or partly from both.

* *Loc. cit.*

Suppose we set r at some fixed value such that on the steepest part of the base characteristic $\frac{r}{R}m > 1$. Evidently there will be some point A on the lower bend of the curve

Fig. 2.



and another point B on the upper bend where $\frac{r}{R}m$ will be unity, or

$$\frac{r}{R}m_A = \frac{r}{R}m_B = 1, \quad \dots \dots \dots (2)$$

and

$$\frac{r}{R} = \frac{1}{m_A} = \frac{1}{m_B}. \quad \dots \dots \dots (3)$$

At points A and B the *total* amplification M is infinitely large, as shown by equations (1) and (2). Thus at point A an infinitesimal increment of E_g' toward the right (fig. 2) causes an increase in I_p . Feed-back action supplies an additional increment to E_g' and this causes a further increase in I_p , and so on. This rise in I_p does not stop at point B as

one might suspect at first, but continues to the point B' where the tangent from A intersects the upper part of the curve, since over this whole range

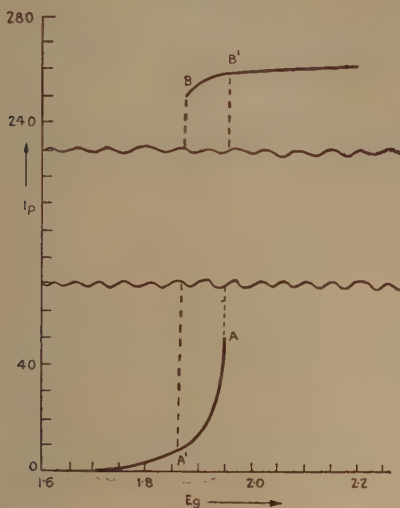
$$\frac{\Delta E_g'}{\Delta I_p} = \frac{1}{m_A} = \frac{r}{R},$$

or

$$\frac{r}{R} \Delta I_p = \Delta E_g',$$

so that the feed-back action alone supplies the requisite grid increment corresponding to the current increment.

Fig. 3.



The plate current I_p becomes stable, however, after reaching B', and remains stable over the whole upper part of the curve as far down as B, since over this region the slope is smaller than at B, so that $\frac{r}{R} m < 1$, and hence according to equation (1) the total amplification is finite. If the current is brought an infinitesimal amount below its value at B it suddenly drops to its value at A' where the tangent from B intersects the lower bend.

If, under the same circuit conditions, we plot the plate current I_p as ordinates and *externally* applied grid (negative) potential E_g as abscissæ, the characteristic takes the form shown in fig. 3, which was drawn from experimental data.

The slope of this curve, in arbitrary units, is the total amplification M . The points A, B', B, and A' represent approximately the same respective plate currents in both fig. 2 and fig. 3. Thus at point A in fig. 2 the slope is

m_A such that $\frac{r}{R} m_A = 1$. By substituting this value of m in

equation (1) we see that the total amplification M_A should be infinite. In fig. 3 it is seen that the slope does approach infinity at A.

The loop A B' B A' A in fig. 3 may be traversed counter-clockwise, but not clockwise since the transitions from A to B' and from B to A' are sudden and irreversible. The other portions of the curve A' A and B B' are stable and reversible. It will be seen that for every externally applied grid potential between A' and A the plate current may have either its value on the lower bend between A' and A or its value on the upper bend between B and B'. Thus previous history determines which value of plate current obtains at any particular value of externally applied grid potential.

LXXV. *On the "Flash" in the After-glow of the Electrodeless Discharge with Change of Pressure.* By CHAS. T. KNIPP, Ph.D., Professor of Experimental Electricity, University of Illinois, and LEE N. SCHEUERMAN, M.A.*

PHENOMENA attending the electrodeless discharge in gases were described many years ago by Sir J. J. Thomson†, who at the time called attention to the phosphorescent glow produced in certain gases and the absence of this glow in others, notably "in a single gas (as distinct from a mixture), unless that gas was one which formed polymeric modifications." This requirement of a mixture, or the trace of another gas as an impurity, was also observed by later investigators. Quite recently Lewis‡ has shown by experiment that absolutely pure oxygen or nitrogen in an uncontaminated out-gassed tube will yield no after-glow. However, if there is a little

* Communicated by the Authors.

† Phil. Mag. ser. 5, xxxii. pp. 321, 445 (1891). 'Recent Researches,' p. 184 (1893).

‡ Journ. Amer. Chem. Soc. li. pp. 654, 665 (1929).

water-vapour present, or if the walls of the tube are contaminated with another gas, an after-glow is formed. Adding a little oxygen to pure nitrogen, or *vice versa*, will give an after-glow. This would indicate the correctness of Thomson's theory referred to above, and extended recently*, in which he states that the after-glow is caused by the formation of systems more easily ionized than the normal gas, rather than by simple recombination of the ionized gas-molecules.

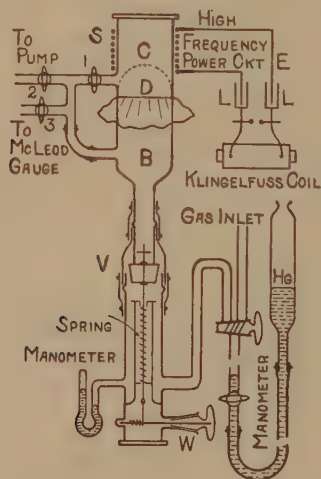
This note has to do with the "flash" that may be made to appear, when the conditions are favourable, in the after-glow on the sudden compression of the glowing gas. It was suggested to one of the writers two years ago, while at the Cavendish Laboratory, by the researches of Sir J. J. Thomson. One of the experiments performed by Sir J. J. Thomson on the lecture table was that, on admitting suddenly a small quantity of gas into the discharge chamber, the after-glow appeared to "flash" momentarily and then faded quickly away. The question naturally arose: What are the conditions that obtain within the tube to produce this flash? Are they brought about in part by the introduction of fresh gas, or may the same flash be obtained by merely compressing the residual gas in the tube, other conditions being favourable?

As a simple initial test the discharge tube was made long, with the exciting high-frequency coil placed at the far end from the gas inlet (this form may also have been used by Sir. J. J. Thomson). Under this arrangement the compression at the exciting end was as by an "air piston." This method of procedure gave quite consistent "flashes."

A more comprehensive test, based on compression only, was planned. The apparatus as ultimately constructed is shown in the figure. C is the discharge chamber, about which is placed the exciting solenoid S of the high-frequency circuit. D is a rubber diaphragm held between the two ground ends of the divided tube, thus separating the compression chamber C from the expansion chamber B. Rubber dental dam was used for D. At the lower end of B is a large-throated valve V for permitting the gas to be introduced quickly into B, and thus causing a sudden

* Phil. Mag. ser. 7, iv. p. 1128 (1927). Proc. Phys. Soc. xl. p. 79 (1928).

compression in C. This large-throated valve consists simply of a rubber stopper mounted on a central rod held firmly against the ground-lip of the tube, extending down from B, by a stiff spring, as shown. Guides are provided to keep the valve central. To the lower end of the valve-stem is attached a winch W which permits opening the valve V quickly. The small manometer gives an indication of the pressure in the system, while the large manometer is used as a means of measuring and regulating the amount of gas being introduced to bring about the



desired compression. The action of this arrangement is apparent from the figure.

The method of operation is to open stopcocks 1, 2, and 3, then lower the valve V by the winch W, and pump the whole system out to the pressure desired. This pressure is read on the gauge. Next stop-cocks 1, 2, and 3, and also the valve V, are closed. The pressures in C and B are the same, and the diaphragm D occupies the unstretched position shown. Gas is now introduced in "doses" through the three-way valve by means of the large manometer until the desired pressure, as indicated by the small manometer, is reached. Everything is now ready for the test. The gas in C is excited by the high-frequency discharge. After

a few moments the exciting current in the solenoid is cut off and the after-glow alone remains. This glow gradually fades; however, before it ceases to be visible, the large-throated valve V is quickly opened and the excited gas in C is suddenly compressed, owing to the excess of pressure in B over that in C. The rubber diaphragm now occupies the position indicated by the dotted line. It is at the end of this sequence that the "flash" in C occurs.

Carrying out the experiment was not at first so simple. Thomson* had observed that some metals, mercury, and, apparently, some non-conductors, seem to kill the after-glow. With the introduction of the rubber diaphragm it was hoped that this difficulty would be eliminated. However, this was not the case; the sulphur in the processed rubber, being electropositive, killed the after-glow. This difficulty was overcome by dipping the dam in pure latex, which contains no sulphur. The coating formed when dry was smooth, and interfered but little with the flexibility of the dam. This covering proved entirely satisfactory—the after-glow seemed to be in no way diminished. That this was the case was thoroughly tested by introducing latex-covered rubber dam into an electrodeless discharge tube specially constructed for testing different substances.

With this annoyance removed, an exhaustive series of experiments was undertaken to determine under what conditions a given gas could be made to "flash." Air, oxygen, and nitrogen were successively worked with. In air the "flash" was noticeable over the whole range of pressures for which the after-glow was visible. In oxygen the "flash" showed the same characteristics. Nitrogen was in marked contrast to oxygen and air. The after-glow in nitrogen, as shown by Thomson, has a maximum life of about 125 seconds. It was very bright, and diminished gradually. The "flash" in nitrogen could be obtained at any time while the after-glow was visible. Its brilliancy seemed to be in direct proportion to the brilliancy of the after-glow. At no time in air, oxygen, or nitrogen, the three gases studied, was a "flash" formed if the compression took place after the after-glow had completely disappeared. An interesting phenomenon in

* Phil. Mag. ser. 7, iv. p. 1128 (1927). Proc. Phys. Soc. xl. p. 79 (1928).

the case of nitrogen was that, following the "flash," the after-glow was still visible, and continued to die out gradually instead of disappearing completely with the flash, as in the case of oxygen. Other interesting results were observed that seemed to be wholly lacking in the case of oxygen; these, however, may have been due to the greater intensity of the after-glow and flash in nitrogen.

A question may be raised as to whether the "flash" here described is really a flash; but, instead, may it not be the uniform illumination of the after-glow compressed into a smaller volume, and thus made to appear brighter? The writers think not. The two cases can readily be distinguished. The "flash" of the after-glow occurs, as seen by the eye, in the form of a flat disk which travels upward from the diaphragm when the gas is suddenly compressed. It seems to accompany a pressure-pulse in the gas. Granting that the after-glow is due to the illumination which accompanies recombination in an ionized gas, we find a plausible explanation of the "flash" in that, on compression, the ions are pushed closer together, which in turn facilitates recombination. On this view no "flash" should result on sudden expansion of the excited gas. Although the effect of expansion has not been exhaustively investigated by the writers, simple preliminary tests indicate that expansion of an ionized gas does not cause a "flash."

ADDENDUM*.

H. F. Newall † investigated pressure conditions in the electrodeless discharge many years ago, and found that in a mixture of two gases (oxygen and nitrogen) the phosphorescence reaches a maximum at about 0.4 mm. Hg, and fades away as the pressure is either increased or decreased from this value. He produced a striking effect by initially adjusting the gas-pressure slightly higher than that for maximum phosphorescence; then, while the gas was glowing, the electrodeless discharge having been cut off, the pressure was suddenly reduced, and he observed a wave of increased brightness travel along the tube toward the

* Newall's experiment, and also Sir J. J. Thomson's account of it, escaped the writers' notice during the progress of this investigation. These were kindly brought to our attention by the Editors after the authors had submitted the MS. for publication.

† Proc. Camb. Phil. Soc. ix. p. 295 (1897).

remote end from the pump. Reasoning from the above, it follows that there should result a wave of diminished brightness if the pressure is suddenly slightly increased. Again, if the pressure is accurately adjusted for maximum brightness, then a wave of diminished brightness should result for *either* a decrease or an increase in pressure. And further, if the pressure is adjusted to a value lower than for maximum brightness, then a reduction in pressure should result in a wave of diminished brightness. In Newall's article mention is made of performing the experiment by causing a reduction in pressure only, his apparatus evidently lending itself better to that case; however, no reference is made to having observed a wave of diminished brightness.

An account of Newall's experiment was given recently by Sir J. J. Thomson* in a lecture before the Société Française des Electriciens in Paris, in which it was shown that there are many cases of luminosity which could not be explained by compression.

In the light of the foregoing, and also of our own results, it seems probable that the alteration in phosphorescence due to change in pressure has two sources: (a) that described by Newall, and later by Thomson, in which the original grouping of the atoms or molecules is no longer stable, and the gas passes into a new state of grouping with the evolution of energy, part of which would account for the "pressure-glow," and which persists for some time; (b) that designated by the term "flash" in this article, whose appearance is only momentary, accompanying a pressure pulse of the residual gas, but not an expansion; it assumes the gas to be ionized, and, granting that compression facilitates recombination, there results an increased illumination. The two types or kinds of phosphorescence are shown in the case of nitrogen, the former continuing for many seconds, the latter for but a moment.

The apparatus sketched in the figure, with slight modifications in the design of chambers C and B, will work equally well on compression or expansion.

* *Supplément au Bulletin de la Société Française des Electriciens*, no. 77, 4th sér., tome 8 (1927).

LXXVI. *The Rotating Electron in a Beam of Light.*
By B. M. SEN, Professor, Presidency College, Calcutta*.

THE theory of Compton effect was investigated by Dirac † using the methods of Heisenberg's matrix mechanics and by Gordon ‡ with Schrödinger's Wave mechanics, with frequent reference to the light-quantum hypothesis and the Correspondence Principle.

It is proposed in the present paper to find a solution of the Wave equation of a rotating electron under a plane polarized beam of light, and indicate the effects.

In 'Nature' of Sept. 15, 1928, Klein and Nishina have given a formula for the intensity of Compton scattering calculated from Dirac's equation. Presumably the method is an extension of that used by Klein in *Zs. f. Phys.* xli. (1927), but the details have not yet been published.

1. Dirac has shown that the Wave equation of a free electron can be written in the form

$$(p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_4 mc)\psi = 0,$$

where the α 's are certain four-rowed matrices, p_1, p_2, p_3 are the components of momentum, and are to be replaced by

$$p_1 = \frac{h}{2\pi i} \frac{\partial}{\partial x}, \quad p_2 = \frac{h}{2\pi i} \frac{\partial}{\partial y}, \quad p_3 = \frac{h}{2\pi i} \frac{\partial}{\partial z},$$

and

$$p_0 = \frac{E}{c} = -\frac{h}{2\pi i} \frac{\partial}{c \partial t}.$$

For an electromagnetic field p_0 is to be replaced by $p_0 + \frac{e}{c}V$, p_1 by $p_1 + \frac{e}{c}A_1$, p_2 by $p_2 + \frac{e}{c}A_2$, p_3 by $p_3 + \frac{e}{c}A_3$, where V is the scalar potential and (A_1, A_2, A_3) is the vector potential.

We take

$$V = 0, \quad A_1 = A_3 = 0, \quad A_2 = a \cos \omega(t - x/c).$$

Taking the values of $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ given by Dirac, we get Darwin's form § of the Wave equations :

* Communicated by the Author.

† Proc. Roy. Soc. cxi. p. 405.

‡ *Zs. f. Phys.* xl. p. 117.

§ Proc. Roy. Soc. cxviii. p. 655.

$$(p_0 + mc)\psi_1 + (p_1 - ip_2')\psi_4 + p_3\psi_3 = 0, \quad . \quad . \quad (1)$$

$$(p_0 + mc)\psi_2 + (p_1 + ip_2')\psi_3 - p_3\psi_4 = 0, \quad . \quad . \quad (2)$$

$$(p_0 - mc)\psi_3 + (p_1 - ip_2')\psi_2 + p_3\psi_1 = 0, \quad . \quad . \quad (3)$$

$$(p_0 - mc)\psi_4 + (p_1 + ip_2')\psi_1 - p_3\psi_2 = 0, \quad . \quad . \quad (4)$$

where $p_2' = p_2 + e'A_2$ and $e' = e/c$.

These, then, are the appropriate Wave equations for a moving electron under a ray of light incident along the x -axis. We note that p_0, p_1, p_2, p_3 , regarded as differential operators, commute with one another. p_2, p_3 commute with A_2 , but p_0 and p_1 do not commute with A_2 .

We shall require the following relations, which are easily verified:—

$$\left. \begin{aligned} \{ (p_1 + ip_2')(p_0 + mc) - (p_0 + mc)(p_1 + ip_2') \} \psi \\ = \{ (p_1 + ip_2')(p_0 - mc) - (p_0 - mc)(p_1 + ip_2') \} \psi \\ = -ie' \psi p_0 A_2, \\ \{ (p_1 - ip_2')(p_0 + mc) - (p_0 - mc)(p_1 - ip_2') \} \psi \\ = \{ (p_1 - ip_2')(p_0 - mc) - (p_0 - mc)(p_1 - ip_2') \} \psi \\ = ie' \psi p_0 A_2, \end{aligned} \right\} \quad (5)$$

$$\left. \begin{aligned} (p_1 + ip_2')(p_1 - ip_2') \psi &= (p_1^2 + p_2'^2) \psi - ie' \psi p_1 A_2, \\ (p_1 - ip_2')(p_1 + ip_2') \psi &= (p_1^2 + p_2'^2) \psi + ie' \psi p_1 A_2. \end{aligned} \right\} \quad (6)$$

2. Multiplying (1) by $p_1 + ip_2'$, (2) by $-p_2$, (4) by $-(p_0 + mc)$, and adding, we have

$$\{ p_1^2 + p_2'^2 + p_3^2 - (p_0^2 - m^2 c^2) \} \psi_4 - ie' \psi_1 p_0 A_2 - ie' \psi_4 p_1 A_2 = 0. \quad . \quad . \quad (7)$$

Similarly from (3), (4), (1) we get

$$\{ p_1^2 + p_2'^2 + p_3^2 - (p_0^2 - m^2 c^2) \} \psi_1 + ie' \psi_1 p_1 A_2 + ie' \psi_4 p_0 A_2 = 0. \quad . \quad . \quad (8)$$

Also from (1), (3), (2) we get

$$\{ p_1^2 + p_2'^2 + p_3^2 - (p_0^2 - m^2 c^2) \} \psi_3 + ie' \psi_3 p_1 A_2 + ie' \psi_2 p_0 A_2 = 0. \quad . \quad . \quad (9)$$

Lastly, from (3), (4), (2) we get

$$\{ p_1^2 + p_2'^2 + p_3^2 - (p_0^2 - m^2 c^2) \} \psi_2 - ie' \psi_3 p_0 A_2 - ie' \psi_2 p_1 A_2 = 0. \quad . \quad . \quad (10)$$

These are equivalent to the differential equations

$$-\frac{h^2}{4\pi^2} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\partial^2}{c^2 \partial t^2} \right] \psi_4 + m^2 c^2 \psi_4 \\ + \frac{h}{2\pi i} \left[2e'a \cos \theta \frac{\partial \psi_4}{\partial y} + ie'u \psi_1 \frac{\partial}{c \partial t} \cos \theta - ie'a \psi_4 \frac{\partial}{\partial x} \cos \theta \right] \\ = 0, \quad \dots \quad (7')$$

$$-\frac{h^2}{4\pi^2} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\partial^2}{c^2 \partial t^2} \right] \psi_1 + m^2 c^2 \psi_1 \\ + \frac{h}{2\pi i} \left[2e'a \cos \theta \frac{\partial \psi_1}{\partial y} + ie'\psi_1 \frac{\partial}{\partial x} \cos \theta - ie'a \psi_4 \frac{\partial}{c \partial t} \cos \theta \right] \\ = 0, \quad \dots \quad (8')$$

where $\theta = \omega(t - x/c)$.

ψ_2 satisfies the same equation as ψ_4 , and ψ_3 as ψ_1 .

3. Since $(\mu_1 - p_0)A_2 = 0$, it is obvious that $\psi_1 + \psi_4$ and $\psi_2 + \psi_3$ also satisfy the differential equation

$$\left(-\frac{h^2}{4\pi^2} \right) \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\partial^2}{c^2 \partial t^2} \right] u \\ + m^2 c^2 u + \frac{h}{2\pi i} 2e'a \cos \theta \frac{\partial u}{\partial x} = 0, \quad (11)$$

neglecting the square of a .

Assume as a solution

$$u \propto e^{\frac{2\pi i}{h} (k_1 x + k_2 y + k_3 z + \lambda ct) + B \sin \theta}, \quad \dots \quad (12)$$

where θ has been put for $\omega(t - x/c)$.

The equation (11) will be satisfied if

$$k_1^2 + k_2^2 + k_3^2 - \lambda^2 + m^2 c^2 = 0 \quad \dots \quad (13)$$

and

$$\frac{h}{\pi i} (k_1 + \lambda) \frac{B\omega}{c} = 2e'ak_2,$$

which gives

$$B = \frac{2\pi i}{h} \frac{e'ack_2}{\omega(k_1 + \lambda)} \quad \dots \quad (14)$$

B is, therefore, a pure imaginary, and is of the same order as a . We can, therefore, write down the solution of (11) in the form

$$u \propto e^{\frac{2\pi i}{h} (k_1 x + k_2 y + k_3 z + \lambda ct)} (1 + B \sin \theta),$$

neglecting the square of a .

4. To find expressions for ψ_1 and ψ_4 separately, we take the equations (7), (8). Assume as a solution

$$\psi_1 = P_1 e^{\frac{2\pi i}{h}(k_1 x + k_2 y + k_3 z + \lambda c t)} (1 + B \sin \theta + C_1 \cos \theta), \quad (15)$$

$$\psi_4 = P_4 e^{\frac{2\pi i}{h}(k_1 x + k_2 y + k_3 z + \lambda c t)} (1 + B \sin \theta + C_4 \cos \theta), \quad (16)$$

where B and the C's are small, and

$$P_1 C_1 + P_4 C_4 = 0.$$

Then

$$\frac{\partial^2 \psi}{\partial x^2} = P_1 \frac{2\pi i}{h} k_1 \left[\frac{2\pi i k_1}{h} (1 + B \sin \theta + C_1 \cos \theta) - \frac{\omega}{c} B \cos \theta + \frac{\omega}{c} C_1 \sin \theta \right] e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)}$$

$$+ P_1 \left[\left(\frac{2\pi i}{h} k_1 B + \frac{\omega}{c} C_1 \right) \left(-\frac{\omega}{c} \cos \theta \right) + \left(\frac{2\pi i}{h} k_1 C_1 - \frac{\omega}{c} B \right) \frac{\omega}{c} \sin \theta \right] e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)},$$

$$\frac{\partial^2 \psi_1}{\partial y^2} = P_1 \left(\frac{2\pi i k_2}{h} \right)^2 (1 + B \sin \theta + C_1 \cos \theta) e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)},$$

$$\frac{\partial^2 \psi_1}{\partial z^2} = P_1 \left(\frac{2\pi i k_3}{h} \right)^2 (1 + B \sin \theta + C_1 \cos \theta) e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)},$$

$$\frac{\partial^2 \psi_1}{c^2 \partial t^2} = P_1 \left(\frac{2\pi i \lambda}{h} \right) \left[\frac{2\pi i \lambda}{h} (1 + B \sin \theta + C_1 \cos \theta) + \frac{\omega}{c} B \cos \theta - \frac{\omega}{c} C_1 \sin \theta \right] e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)}$$

$$+ P_1 \left[\left(\frac{2\pi i}{h} \lambda B - \frac{\omega}{c} C_1 \right) \frac{\omega}{c} \cos \theta + \left(\frac{2\pi i \lambda}{h} C_1 + \frac{\omega}{c} B \right) \left(-\frac{\omega}{c} \sin \theta \right) \right] e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)},$$

$$2e'a \cos \theta \cdot \frac{h}{2\pi i} \frac{\partial \psi_1}{\partial y} = 2e'ak_2 \cos \theta P_1 e^{\frac{2\pi i}{h}(k_1 x + \dots + \lambda c t)},$$

$$\frac{h}{2\pi i} \left[ie'a \psi \frac{\partial}{\partial x} \cos \theta - ie'a \psi_4 \frac{\partial}{c \partial t} \cos \theta \right] = \frac{he' \omega a}{2\pi c} (P_1 + P_4) \sin \theta.$$

Substituting in equation (8'), and putting the finite terms and the coefficients of $\cos \theta$ and $\sin \theta$ separately to zero, we have the relation (13), the value of B found before (14), and

$$P_1 C_1 = -\frac{ie'a(P_1 + P_4)}{2(k_1 + \lambda)} \dots \dots \dots (17)$$

We have, therefore,

$$P_4 C_4 = \frac{ie'a(P_1 + P_4)}{2(k_1 + \lambda)} \dots \dots \dots (17')$$

And similarly,

$$P_2 C_2 = -P_3 C_3 = \frac{ie'a(P_2 + P_3)}{2(k_1 + \lambda)} \dots \dots \dots (18)$$

5. The relations between P_1, P_2, P_3, P_4 are obtained by substituting the values of ψ_1 and ψ_4 given by (15), (16) and two similar expressions for ψ_2, ψ_3 in equations (1)-(4). We thus obtain

$$(-\lambda + mc)P_1 + (k_1 - ik_2)P_2 + k_3 P_3 = 0, \dots \dots (19)$$

$$(-\lambda + mc)P_2 + (k_1 + ik_2)P_3 - k_3 P_4 = 0, \dots \dots (20)$$

$$(-\lambda - mc)P_3 + (k_1 - ik_2)P_4 + k_3 P_1 = 0, \dots \dots (21)$$

$$(-\lambda - mc)P_4 + (k_1 + ik_2)P_1 - k_3 P_2 = 0, \dots \dots (22)$$

Also, the first approximation terms give

$$\begin{aligned} P_1 C_1 \{ (-\lambda + mc) - (k_1 - ik_2) \} + k_3 P_3 C_3 \\ = \frac{\hbar}{2\pi i} (P_1 + P_4) \frac{B\omega}{c} + \frac{ie'}{a} P_4, \end{aligned} \quad (23)$$

$$\begin{aligned} P_2 C_2 \{ (-\lambda + mc) - (k_1 + ik_2) \} + k_3 P_4 C_4 \\ = \frac{\hbar}{2\pi i} (P_2 + P_3) \frac{B\omega}{c} - \frac{ie'}{a} P_3, \end{aligned} \quad (24)$$

with

$$P_1 C_1 + P_4 C_4 = 0, \quad P_2 C_2 + P_3 C_3 = 0,$$

and

$$k_1^2 + k_2^2 + k_3^2 - \lambda^2 + m^2 c^2 = 0.$$

These relations are not all independent. It is easily verified that if we substitute the values of $P_1 C_1$ and $P_3 C_3$ in (23) we get

$$(P_1 + P_4) \{ (-\lambda + mc) - (k_1 + ik_2) \} + k_3 (P_2 + P_3) - 2P_4 (k_1 + \lambda),$$

which is an identity by virtue of equations (19), (23). We may take for the independent relations the equations (13), (14), (17), (17'), (18) and two out of the four equations (19)-(22).

We proceed to find expressions for the components of the stream-vector.

6. The stream vector * is given by the equations

$$\rho = -e\{\psi_1'\psi_1 + \psi_2'\psi_2 + \psi_3'\psi_3 + \psi_4'\psi_4\}, \quad . \quad . \quad (25)$$

$$j_1 = ce\{\psi_1'\psi_4 + \psi_2'\psi_3 + \psi_3'\psi_2 + \psi_4'\psi_1\}, \quad . \quad . \quad (26)$$

$$j_2 = ce\{-i\psi_1'\psi_4 + i\psi_2'\psi_3 - i\psi_3'\psi_2 + i\psi_4'\psi_1\}, \quad . \quad (27)$$

$$j_3 = ce\{\psi_1'\psi_3 - \psi_2'\psi_4 + \psi_3'\psi_1 - \psi_4'\psi_2\}, \quad . \quad . \quad (28)$$

ψ_1' being the imaginary conjugate to ψ_1 , the Wave functions being so normalized that

$$\int (\psi_1'\psi_1 + \psi_2'\psi_2 + \psi_3'\psi_3 + \psi_4'\psi_4) dx dy dz = 1.$$

For the plane Wave solution, which has been taken as the basis, normalizing has no significance. For a plane de Broglie wave the density must be supposed to be distributed uniformly over the whole space †.

7. Denoting by $(\rho)_0$ the value of ρ when a is put equal to zero, *i. e.* the finite terms of ρ , and by $(\rho)_1$ the small terms of the first order, we have

$$\left(-\frac{\rho}{e}\right)_0 = \{P_1'P_1 + P_2'P_2 + P_3'P_3 + P_4'P_4\}.$$

From (19), (20),

$$P_1 = \frac{k_1 - ik_2}{\lambda - mc} P_4 + \frac{k_3}{\lambda - mc} P_3, \quad P_1' = \frac{k_1 + ik_2}{\lambda - mc} P_4' + \frac{k_3}{\lambda - mc} P_3', \quad . \quad . \quad (29)$$

$$P_2 = \frac{k_1 + ik_2}{\lambda - mc} P_3 - \frac{k_3}{\lambda - mc} P_4, \quad P_2' = \frac{k_1 - ik_2}{\lambda - mc} P_3' - \frac{k_3}{\lambda - mc} P_4', \quad . \quad . \quad (30)$$

Substituting these values, and simplifying,

$$\left(-\frac{\rho}{e}\right)_0 = \frac{2\lambda}{\lambda - mc} (P_3P_3' + P_4P_4'). \quad . \quad . \quad (31)$$

* Darwin, Proc. Roy. Soc. cxviii. p. 660 (1928).

† Cf. Sommerfeld, 'Atombau und Spektrallinien, Wellenmechanischer Ergänzungsband,' p. 287.

Remembering that B is a pure imaginary, we have from (25)

$$\begin{aligned} \left(-\frac{\rho}{e}\right)_1 &= [P_1 P_1' (C_1 + C_1') + P_2 P_2' (C_2 + C_2') \\ &\quad + P_3 P_3' (C_3 + C_3') + P_4 P_4' (C_4 + C_4')] \cos \theta \\ &= 2iQ [P_1 P_4' - P_1' P_4 + P_2' P_3 - P_3' P_2] \cos \theta \\ &= \frac{4k_2 Q}{\lambda - mc} (P_3 P_3' + P_4 P_4') \cos \theta, \quad . \quad . \quad . \quad (32) \end{aligned}$$

where $Q = e'a/2(k_1 + \lambda)$.

Similarly,

$$\left(\frac{j_1}{ce}\right)_0 = \frac{2k_1}{\lambda - mc} (P_3 P_3' + P_4 P_4'), \quad . \quad . \quad . \quad (33)$$

$$\left(\frac{j_2}{ce}\right)_0 = \frac{2k_2}{\lambda - mc} (P_3 P_3' + P_4 P_4'), \quad . \quad . \quad . \quad (34)$$

$$\left(\frac{j_3}{ce}\right)_0 = \frac{2k_3}{\lambda - mc} (P_3 P_3' + P_4 P_4'), \quad . \quad . \quad . \quad (35)$$

which have the obvious meaning that in the absence of the electromagnetic field the current at any point is in the direction of the plane wave. Proceeding to the first approximation, we have

$$\begin{aligned} \left(\frac{j_1}{ce}\right)_1 &= [P_1' P_4 (C_1' + C_4) + P_4' P_1 (C_4' + C_1) \\ &\quad + P_2' P_3 (C_2' + C_3) + P_3' P_2 (C_3' + C_2)] \cos \theta \\ &= 2iQ [P_1' P_4 - P_4' P_1 + P_2 P_3' - P_2' P_3] \cos \theta \\ &= -\frac{4Qk_2}{\lambda - mc} (P_3 P_3' + P_4 P_4') \cos \theta, \quad . \quad . \quad . \quad . \quad (36) \end{aligned}$$

$$\begin{aligned} \left(\frac{j_2}{ce}\right)_1 &= [-iP_1' P_4 (C_1' + C_4) + iP_4' P_1 (C_4' + C_1) \\ &\quad + iP_2' P_3 (C_2' + C_3) - iP_3' P_2 (C_3' + C_2)] \cos \theta \\ &= 2Q [(P_1 + P_4) (P_1' + P_4') + (P_2 + P_3) (P_2' + P_3')] \cos \theta \\ &= \frac{4Q(\lambda + k_1)}{\lambda - mc} (P_3 P_3' + P_4 P_4') \cos \theta, \quad . \quad . \quad . \quad . \quad (37) \end{aligned}$$

$$\begin{aligned} \left(\frac{j_3}{ce}\right)_1 &= [P_1' P_3 (C_1' + C_3) + P_3' P_1 (C_3' + C_1) \\ &\quad - P_2' P_4 (C_2' + C_4) - P_4' P_2 (C_4' + C_2)] \cos \theta \end{aligned}$$

$$\begin{aligned}
&= iQ[P_3(P_1' + P_4') - P_1'(P_2 + P_3) + P_1(P_2' + P_3') \\
&\quad - P_3'(P_1 + P_4) + P_4(P_2' + P_3') - P_2'(P_1 + P_4) \\
&\quad + P_2(P_1' + P_4) - P_4'(P_2 + P_3)] \cos \theta \\
&= 0. \quad \dots \dots \dots (38)
\end{aligned}$$

We get, therefore,

$$\begin{aligned} j_1 : j_2 : j_3 &= 2k_1 - 4Qk_2 \cos \theta : 2k_2 + 4Q(\lambda + k_1) \cos \theta : 2k_3 \\ &= 2k_1 - \frac{2k_2 e' a}{\lambda + k_1} \cos \theta : 2k_2 + 2e' a \cos \theta : 2k_3. \quad (39) \end{aligned}$$

Thus there is an impulse not only in the direction of the ray, as in the light-quantum hypothesis, but also in the direction of the electrical force, but none in the direction of the magnetic force. If we generalize the solution (15), (16) after Fourier, we get expressions for the stream-vector in the same form as Gordon's.

8. It would be interesting to compare these expressions with those of Gordon. His expression* for the stream-vector runs as

$$S_a = \frac{2\pi}{h} \int \{ \sigma p_a + (\pi_a \sigma k - 2b_a) \cos \phi \} e^{\frac{2\pi i}{h} \delta W} z(p) z(p') C(p) C(p') dp dp', \quad (40)$$

with his own notation. The expression within the curly brackets reduces to the following, if we allow for the difference in the notation :---

$$\left. \begin{aligned} j_1 & 2k_1 + \frac{2k_2 e' a}{\lambda + k} \cos \theta, \\ j_2 & 2k_2 - 2e' a \cos \theta, \\ j_3 & 2k_3. \end{aligned} \right\} \cdot \cdot \cdot \cdot (41)$$

The factors $z(p)$, $C(p)$ are the Fourier generalizing factors. These expressions differ from (39) in having opposite signs in the effective terms.

These relations may give interesting comparisons with Klein and Nishin's work when the details are available

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* Gordon, *Zs. f. Phys.* xl. p. 126 (1927).

LXXVII. *On the Structure of Serial Relations.*

By D. M. WRINCH, M.A., D.Sc.†

IN some papers in the *Berichte der mathematisch physischen Klasse der Königlich Sächsischen Gesellschaft der Wissenschaften zu Leipzig* ‡, Hausdorff has introduced the notion of the element and gap characters of a series of terms. By means of it interesting facts about the nature of the more complicated serial types can be obtained. The theory of series, in general, deals only with Dedekindian series, with series having Cantorian continuity as a subclass of these, with well-ordered series, and with rational series. Dedekindian series, it may be recalled, are defined as series which are compact and Dedekindian: a series is compact if between every two terms there is another term, and a series is Dedekindian if every segment has a sequent. Rational series are defined as series which are compact, have no beginning or end, and consist of an enumerable infinity of terms: they are ordinally similar to the series of rational proper fractions arranged in order of magnitude. Series are said, further, to have Cantorian continuity if they are Dedekindian series and contain a rational series in such a way that there are terms of the rational series between any two terms; they are ordinally similar to the series of real numbers in order of magnitude, including 0 and ∞ . Well-ordered series are defined as those series in which every existent class contained in them has a first term: the series of integers in order of magnitude provides an example of a well-ordered series.

The theory of the element and gap characters of series deals, however, not only with these well-known types of series: it suggests innumerable further serial types, and indeed directs attention to the fact that, so far, only the simplest kinds of serial types have received any attention in technical mathematics and that the nature of serial types in general is a practically untouched field.

A term x of a series P is said to be a (ν, μ) element, where ν and μ are less than ω , if there is an ω_μ series contained in P having x as its upper limit, and an $\ast\omega_\nu$ series contained in P having x as its lower limit. Thus the term $\frac{1}{2}$ in the series of fractions arranged in order of magnitude has

† Communicated by the Author.

‡ "Untersuchungen über Ordnungstypen," 1906 and 1907.

the character $(0, 0)$, since there is an ω_0 (generally written ω) contained in the series, *e. g.*,

$$3/8, 7/16, \dots (2^{n+1} - 1)/2^{n+2}, \dots,$$

which has $\frac{1}{2}$ as its upper limit, and an $^*\omega_0$ (generally written $^*\omega$) contained in the series, *e. g.*,

$$\dots (2^{n+1} + 1)/2^{n+2}, \dots 9/16, 5/8,$$

which has $\frac{1}{2}$ as its lower limit. If it is assumed that the same term cannot be the upper limit of an ω_m and an ω_n in the same series unless $m = n$, it would follow that the element character of any term is unambiguously defined. It should, however, be recorded that this assumption, though it is almost universally adopted, has not yet been proved without the Multiplicative Axiom †.

For convenience we can bring the notion of a term of a series being the limit of an ω_μ and being also the last term of a series under the notion of a (ν, μ) term. For we have the convention that the last term of a series is the lower limit of the null class with respect to the series; so introducing the *ad hoc* definition of ω_z as the ordinal type of a series whose field is the null class \wedge , we are able to systematize such a term as being a (z, μ) element. Similarly, we systematize the first term of a series which is the lower limit of an $^*\omega_\nu$ as a (ν, z) element.

Thus we have, adopting throughout the notation of 'Principia Mathematica,'

$$\begin{aligned} x\epsilon(\nu, \mu)_P &:= : (\exists R, S). R, S \epsilon Rl'P. R\epsilon\omega_\mu. S\epsilon^*\omega_\nu. \text{seq}_P'C'R \\ &= x = \text{prec}_P'C'S \quad . \quad . \quad (\text{Df}) \end{aligned}$$

as the definition of what is meant by saying that a term x in a series P has the element character (ν, μ) . Then, since the last term of a series is the lower limit of the null class with respect to the series ‡,

$$B\check{P} = \text{prec}_P'\wedge.$$

Introducing the definition of ω_z in the form suggested, namely,

$$\omega_z = 0_r,$$

we deduce that

$$^*\omega_z = 0_r$$

† See 'Principia Mathematica,' *265.

‡ See 'Principia Mathematica,' *207.17.

also. It follows, then, that

$$x \in (z, \mu)_P = (\exists R, S). R, S \in Rl' P. R \in \omega_\mu. S \in 0_r. \text{seq}_P ' C' R \\ = x \text{ prec} ' C' S,$$

which implies, since a 0_r has \wedge as its field, that

$$x \in (z, \mu)_P = (\exists R). R \in P. R \in \omega_\mu. \text{seq}_P ' C' R = x = \text{prec} ' \wedge,$$

and consequently that

$$x \in (z, \mu)_P = x = B' \check{P}. (\exists R). R \in P. R \in \omega_\mu. x = \text{seq}_P ' R.$$

The interpretation of a (z, μ) element and a (ν, z) element is therefore achieved.

It will, further, be convenient to systematize the cases which arise when a term in a series has an immediate successor or predecessor. Since Hausdorff deals only with compact series, the case of consecutive terms does not arise in his work.

Let us call a term which is the upper limit of an ω_μ and has an immediate successor a $(-1, \mu)$ element, and a term which is the lower limit of an $^*\omega_\nu$ and has an immediate predecessor a $(\nu, -1)$ element. A term which has an immediate predecessor and an immediate successor would be called a $(-1, -1)$ element. These definitions are convenient, as they enable us in specifying the element characters of the terms of a series to specify not only the kinds of well-ordered series and converses of well-ordered series of which terms of the series are limits, but also the existence of consecutive terms. The use of the index -1 in such cases can be legitimized by the introduction of the convention that

$$\omega_{-1} = s'NO \text{ fin},$$

which involves also that

$$^*\omega_{-1} = s'NO \text{ fin}.$$

From this definition the interpretation of the index as denoting an immediate predecessor or successor easily follows.

For suppose that x is an ω_μ limit, but has an immediate successor. Then

$$(\exists R). R \in \omega_\mu. x \text{ prec}_P ' C' R. (\exists y). x P_y. R \in Rl' P,$$

so that

$$(\exists R, S). R, S \in Rl' P. R \in \omega_\mu. S \in 1. \text{prec}_P ' C' R = x = \text{prec}_P ' C' S.$$

It then follows that

$$x \in (-1, \mu)_P.$$

It will be convenient also to introduce the definition

$$(\nu, \mu) \in \text{elt}' P = (\exists x). x \in (\nu, \mu)_P. \quad \dots \quad (\text{Df})$$

To illustrate the ideas here defined, we may consider the element characters of various well-known serial types. An ω_1 series has a $(-1, z)$ element, since it has a first term which has an immediate successor. It also has $(-1, 1)$ elements, and, since it has a term which is an ω limit and has an immediate successor, a $(-1, 0)$ element. The fact that the left-hand member in each case is -1 expresses the fact that each term in the series has an immediate successor: this is one of the marks of a well-ordered series. Finally, the fact that the right-hand members are -1 or 0 , shows that the series contains no series greater than an ω , and the non-occurrence of z on the left denotes that the series has no end. An ω_2 would have as element characters

$$(-1, 1), (-1, 0), (-1, -1), (-1, z),$$

and an ω_3 the element characters

$$(-1, 2), (-1, 1), (-1, 0), (-1, -1), (-1, z),$$

and so on. A rational series with ends has element characters

$$(z, 0), (0, 0), (0, z).$$

An interesting point emerges when we consider the element characters of a series which possesses Cantorian continuity. Evidently its only element characters are

$$(z, 0), (0, 0), (0, z),$$

and these are those possessed by a rational series.

The specification of the element characters of a series takes no account of whether or not there are series of ascending or descending ordinal types which are not limited, *i. e.*, which do not possess limits among the terms of the series; and this is where a rational series with Cantorian continuity differs: for a rational series contains ω and $^*\omega$ series without limits, whereas in a series with Cantorian continuity all ω and $^*\omega$ series have limits. We therefore make use of Hausdorff's concept of the gap characters of a series.

A series P will be said to have a (ν, μ) gap, if there is an ω_μ and an $^*\omega_\nu$ contained in P such that any term of the series following the whole of the ω_μ follows at least one member of the $^*\omega_\nu$, and any term of the series preceding the whole of the $^*\omega_\nu$ precedes at least one member of the ω_μ . Just as we had the case of a term of a series being an ω_μ limit, and being the last term of a series, so now we have the case of there being in a series P , a series which is an ω_μ

and which is such that no term of the series follows all the ω_μ series. And using the definition already introduced for ω_z , we can bring this case under the case of a (ν, μ) gap. For we have

$$(\nu, \mu) \in \text{gap}' P : = : (\exists R, S). R \epsilon \omega_\mu. S \epsilon^* \omega_\nu. R. S \epsilon Rl' P \\ .p' \vec{P}'' C' S \subset P'' C' R. p' \vec{P}'' C' \subset \vec{P}'' C' S. \quad (\text{Df})$$

P is then "confinal" with an ω_μ if

$$(\exists R). R \epsilon Rl' P. R \epsilon \omega_\mu. p' \vec{P}'' C' R \subset \wedge. C' P \subset P'' C' R,$$

that is, if

$$(\exists R, S). R \epsilon Rl' P. R \epsilon \omega_\mu. C' S = \wedge. p' \vec{P}'' C' R \subset C' S \\ .p' \vec{P}'' C' S \subset P'' C' R,$$

that is, if

$$(\exists R, S). R, S \epsilon Rl' P. R \epsilon \omega_\mu. S \epsilon \omega_z. p' \vec{P}'' C' R \subset C' S \\ .p' \vec{P}'' C' S \subset P'' C' R,$$

that is, if

$$(z, \mu) \in \text{gap}' P.$$

In the same way, P is "co-initial" with an $^* \omega_\nu$ if

$$(\nu, z) \in \text{gap}' P.$$

We may therefore follow Hausdorff and introduce the following definitions:—

$$P \text{ conf } \omega_\mu = (z, \mu) \in \text{gap}' P, \quad . . . \quad (\text{Di})$$

$$P \text{ co-in } ^* \omega_\nu = (\nu, z) \in \text{gap}' P. \quad (\text{Df})$$

It will be remarked that rational and continuous series which share a trio of element characters may be differentiated by means of their gap characters.

On the basis of the definitions it proves feasible to analyse the nature of serial types in general. It is noteworthy that the series usually discussed can be so conveniently specified by means of element and gap characters. But the importance of the ideas resides in the fact that they afford a method of continuity and of generalizing it, and indeed suggest various lines of investigation which yield results belonging to the theory of serial structure. These will be given in other communications.

Lady Margaret Hall,
Oxford,
October 3, 1929.

LXXVIII. *Changes in the Dimensions of Metallic Wires produced by Torsion.*—I. *Soft Drawn Copper.* By THOMAS LONSDALE, M.Sc. (London), F.Inst.P., British Silk Research Association*.

Summary.

THE paper gives measurements of the changes in length of "high conductivity" soft drawn copper wire which occur while the wire is being twisted at room temperature, the wire being under a constant load which is small in comparison with the load necessary to produce permanent set. Considerable elongations are produced even under very small tensions; for somewhat larger tensions much greater elongations are produced for the same degree of twist.

If e is the elongation as a percentage of the initial length, T the twist put in in turns per cm., t the initial tension in kg. per sq. cm., D the diameter in cm., then the expression $e = 4.9 DT(1 + 0.0065 t)$ roughly gives the relationship existing within the limits of 0.105 for DT , and 10–500 for t , for values of D of 0.071, 0.037, 0.023 and 0.012 cm. The wire is apt to break when an elongation of 3–4 per cent. is reached, but elongations of 1–0.12 per cent. have been observed. For insufficiently annealed wire the elongations are rather smaller, while hard drawn copper wire contracts as much as 1 per cent. on twisting under small tensions.

IN 1906 Ercolini⁽¹⁾ found that cycles of torsion applied to a loaded copper wire caused the wire to elongate.

Later, Poynting⁽²⁾ showed mathematically that a perfectly elastic solid of cylindrical form when subjected to a pure torsional shear experiences a small elongation which is proportional to the square of the twist. Working within the torsional elastic limit, he verified this prediction for hard drawn copper and steel wires⁽³⁾, and for one turn of twist in a length of 160.5 cm. found the elongation to be 6.81×10^{-4} cm. for a copper wire of diameter 0.1219 cm. and 4.66×10^{-4} cm. for a steel wire of diameter 0.1210 cm.;

* Communicated by the Author.

he found the permanent set in these wires to be very considerable for three turns of twist.

In the experiments now described the changes in length were measured which occur when "high conductivity" soft drawn copper wire under various tensions is twisted until the breaking-point is reached.

The tensions applied were too small to produce measurable elongations when acting alone in the absence of torsion, and as the elongations within the torsional elastic limit studied by Poynting are less than can be measured by the apparatus employed, the considerable elongations observed (5-10 per cent.) are those produced in the post elastic state of the material by the combined action of the torsion and the tension. The measurements were made at room temperatures.

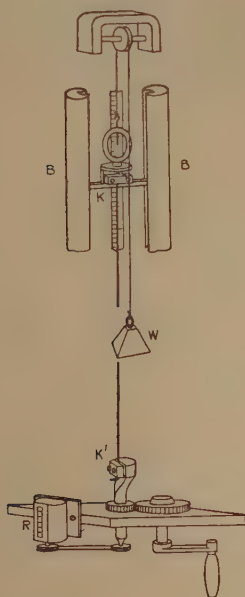
Apparatus and Method.

The apparatus is shown diagrammatically in fig. 1. The wire under observation is mounted vertically between an upper clamp K and a lower clamp K'. The upper clamp K hangs from a thread which, passing over a pulley, sustains at its other end the weights W to balance the weight of the clamp and exert any desired tension on the wire; the clamp can move freely up and down, but is prevented from rotating by an attached horizontal brass bar, the ends of which lie in "key ways" milled in two cylindrical shafts B which are mounted vertically in a fixed position. The lower clamp K' is mounted so that it can experience only a rotational movement round a vertical axis. The wire is twisted by rotating this lower clamp, which is fitted with a revolution counter R to record the number of turns of twist introduced into the wire. In order to ascertain whether the wire turns in either clamp during twisting, the wire is passed right through the clamp and then bent at right angles. No movement of the bent end relative to the clamp was observed in any experiment.

The jaws of the clamps are faced with cardboard for the finer wires, and with leather for the thicker ones; if the jaws are not faced, the wires tend to break at the clamps at abnormally low values of the twist and extension. Even with the faced jaws the wire may break at one or other of the clamps, but when this happens with the faced jaws the twist and extension at break are not much less than when the wire happens to break in the middle.

The initial length of wire between the clamps was usually 1.75 metres. The changes in length corresponding to successive equal increments of twist as recorded on the revolution counter were read off in terms of the movement of the upper clamp by means of a vertical scale fixed to the steel shafts.

Fig. 1.



Tensions employed.

In these experiments the tensions employed ranged from 9–515 kg. per sq. cm. They were less than those required to produce a measurable extension in the absence of torsion during the time occupied by the experiment.

In the absence of torsion a tension of 515 kg. per sq. cm. acting for 24 hours produced no measurable elongation of the copper wires. The elastic limit of annealed copper is given by Tammann⁽⁴⁾ as 203 kg. per sq. cm., but measurements made by Andrade⁽⁵⁾ show that the elongation of soft drawn copper wire is extremely small for tensions

considerably greater than this. This was confirmed for the material used in the present experiments. Thus a length of copper wire of diameter 0.0375 cm., under a tension of 1020 kg. per sq. cm. but not subjected to torsion, showed an initial elongation of 0.14 per cent. and a further elongation of 0.05 per cent. after 24 hours. The tensile strength of annealed copper wire is about 3000 kg. per sq. cm.

The considerable extensions produced by twisting under tensions far below the elastic limit recorded by Tammann are indicated in Table I., in which a few of the results obtained are summarized.

TABLE I.

Extension of Copper Wires on twisting.

D = diameter of the wire in cm.

L = load in grams.

t = initial tension in kg. per sq. cm.

T = twist in turns per cm. of the initial length.

e = the corresponding elongation per cent. of the initial length.

D=0.0715 (22 S.W.G.).

L ... 40 ... 260 ... 510

t ... 10 ... 65 ... 127

T.	e .	e .	e .
2	0.69	1.10	1.54
4	1.81	2.38	3.01
6	2.92	3.74	4.58
8	3.99	4.97	6.05
10	4.85	6.00	7.29
12	5.50		8.30
14	5.99		9.13

D=0.0375 (28 S.W.G.).

L ... 10 ... 70 ... 140

t ... 9 ... 64 ... 127

T.	e .	e .	e .
4	0.59	0.88	1.27
8	1.31	1.83	2.46
12	2.08	2.78	3.66
16	2.76	3.68	4.75
20	3.31	4.42	5.70
24	3.72	5.00	6.49
28		5.46	

D=0.0230 (34 S.W.G.).

L ... 4 ... 26 ... 53

t ... 10 ... 63 ... 128

T.	e .	e .	e .
6	0.50	0.77	1.07
12	1.21	1.67	2.23
18	1.93	2.54	3.32
24	2.55	3.33	4.29
30		4.01	5.15
36		4.57	

D=0.012 (40 S.W.G.).

L ... 1 ... 7 ... 14

t ... 9 ... 62 ... 124

T.	e .	e .	e .
10	0.48	0.66	0.95
20	1.21	1.57	2.10
30	2.01	2.53	3.26
40	2.73	3.39	4.31
50	3.33	4.13	5.23
60	3.80		5.97

The results in Table I. show that the dependence of the extension upon the tension is quite large, even for small tensions. In Table I. the lowest tension employed (9-10 kg. per sq. cm.) is only just enough to give the wire an approach to straightness before twist is introduced. The first few turns of twist in the 1.75-metre lengths (not turns per cm.) have the effect of straightening the wire, thus enabling measurements to be obtained, yet even for this very small tension the elongations produced by further twisting are quite large.

In Table II. the extension obtained by the action of tension alone is compared with that obtained by tension and torsion.

TABLE II.

Comparison of Tension alone and of Tension + Torsion required to produce a given Elongation (Annealed Copper Wire).

	Diameter 0.0444 cm. Without twist. (Andrade.)	Diameter 0.0375 cm. Twist 24 turns per cm. (from Table I.).
Tension (kg./sq. cm.).....	1696	9
Elongation (per cent. of initial length).	$\begin{cases} 3.7 \text{ immediate;} \\ 5.9 \text{ after } \frac{1}{2} \text{ hour.} \end{cases}$	3.7

Discussion of the Results.

Some of the results obtained are shown graphically in fig. 2, which gives the twist-extension curves for approximately the same range of tensions for wires of four diameters.

These curves show some remarkable features. The general appearance of the four sets suggests that they belong to the same family, and that the phenomenon under consideration is therefore a definite physical effect; the elongation produced by a given amount of twist is strikingly dependent upon the diameter of the wire and its tension. These factors are discussed separately.

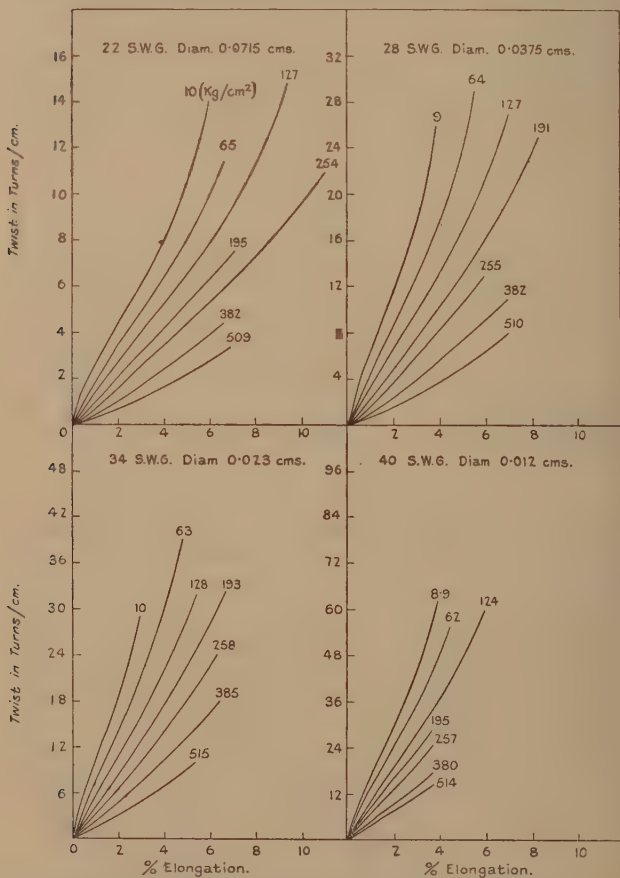
Effect of Diameter of Wire.

The diameters of the four wires employed are in the ratio of (approximately) 6 : 3 : 2 : 1. In the curves the scales of "twist" have been adjusted to be in the same ratio, that is, the scale of the first set is twice that of the second, three times that of the third, and six times that of

the fourth. It will be seen that in this way the four sets of curves are made comparable; they occupy approximately the same space. In other words, the elongation

Fig. 2.

Twist-extension Curves for Soft Drawn Copper Wire of various Diameters under various Tensions.



(The number at the top of each curve is the initial tension on the wire in kg./sq. cm.)

for a given twist and a given tension is roughly proportional to the diameter of the wire. The mean percentage

elongations at which break takes place for the four sets of curves, namely 7·7, 6·4, 5·5, 4·2, show that the thinner wires tend to break at a less extension than the thicker ones, but that the tendency to break is by no means proportional to the diameter of the wire.

Effect of Tension applied to Wire.

As the wire elongates, its diameter decreases slightly and the tension corresponding to a given load therefore increases. This increase, however, is only a matter of a few parts per cent. and has been neglected.

With increasing tension the elongation increases, but the proportionality is by no means direct. The curves also change their shape in each of the four sets of curves. For low tensions (such that initial twist is required to straighten out the wires) the curves are slightly S-shaped, the rate of extension per unit twist being greatest towards the middle of the curve. For the highest tensions employed, the lower part of the S has disappeared and the rate of extension per unit twist is greatest at the origin. In the case of the thinner wires the high-tension curves are practically straight lines. No attempt to express these facts by means of a definite family formula has met with any great success. Neglecting the sinuosity of the curves, it may be stated empirically that the percentage elongation e varies approximately as $(1+0\cdot0065\ t)$, where t is the initial tension in kg./sq. cm.

Effect of Twist applied to Wire.

For a given diameter and applied tension the percentage elongation increases almost directly with the amount of twist. This again neglects the sinuous character of the curves, which are assumed to be nearly linear, as indeed they are for low diameters and high tensions.

An approximate formula covering the whole family of curves is :—

$$e = k \cdot DT (1 + 0\cdot0065\ t), \quad . \quad . \quad . \quad (A)$$

where e is the elongation expressed as a percentage of the initial length of the wire,

D is the diameter in cm.,

T the twist in turns per cm.,

t the initial tension in kg. per sq. cm.

TABLE III. (*cont.*).

Experimental Values of the Constant k in the
Expression $e = k DT(1 + 0.0065 t)$.

D=0.012 cm. 40 S.W.G.														
L	...	1	...	7	...	14	...	22	...	29	...	43	...	58
<i>t</i>	...	9	...	62	...	124	...	195	...	257	...	380	...	514
DT.		<i>k.</i>		<i>k.</i>		<i>k.</i>		<i>k.</i>		<i>k.</i>		<i>k.</i>		<i>k.</i>
0.150		4.0		4.1		4.5		4.4		4.5		5.0		5.0
0.300		5.1		4.9		4.9		4.7						
0.450		5.4		5.0		5.0								
0.600		5.4		4.9		4.8								
0.750		4.9												

The mean value of k computed from this table is 4.9.
The approximate expression is thus

$$e = 4.9 DT(1 + 0.0065 t)$$

within the limits of 0.1-0.5 for DT, and 10-500 kg. per sq. cm. for t , for values of D of 0.071, 0.037, 0.023, and 0.012 cm.

The wires are apt to break for values of e greater than 3-4 per cent., though elongations of as much as 12 per cent. have been obtained.

Changes in Diameter.

Concurrently with the elongation of the wires that occurs on twisting, a decrease occurs in the diameter as measured by a screw gauge; but this decrease of diameter is less than would be required to maintain constancy of volume, and the density calculated from these measurements therefore shows a decrease which may be as much as 1 per cent. after severe twisting. The decrease of density actually observed, using a density bottle, with six specimens of wire on twisting severely, was only one-third per cent. (mean relative density at 25°/4° C. of the untwisted wire 8.93; of the twisted wire 8.90). This discrepancy finds a ready explanation in the regular distortion of the surface of the wire that occurs on twisting into fine parallel spiral ridges and depressions; the diameter measured by the gauge is, of course, that of the ridges. An examination of these spirals, which present a beautiful effect when viewed microscopically, shows that the twist distributes itself fairly uniformly along the wire.

Annealing.

In the case of fine wires of soft drawn copper, the necessary winding after the wire leaves the annealing furnace is known to harden the wire. In order to see if the wire to be used was quite soft, a skeleton series of twist-extension experiments was made on each "gauge" of wire used, first as purchased, and then after annealing in oil for 15 minutes at 300°C . and cooling slowly⁽⁶⁾. No differences were found in the results, except in the case of the finest wire used (diameter 0.012 cm.), which for the same twist showed increased elongations after annealing. Hard drawn copper wire under small tensions shows a contraction in length on torsion which may be as much as 1 per cent. As a check on the efficacy of the annealing, a length of hard drawn copper wire annealed with the soft drawn copper gave subsequent results on twisting identical with those of the soft drawn copper. In the main series of experiments the wires were used as purchased, with the exception of the finest wire, which was annealed as described above before use.

Accuracy of the Results.

Repetition of some of the measurements showed that the elongations of different portions of wire from the same coil, under the same tension for a given twist, did not vary by more than one part in twenty; the variation was usually much less than this.

Preliminary Experiments made to detect some possible Causes of Error.

Andrade (*loc. cit.*), referring to wires of lead and soft drawn copper, remarks: "Large preliminary strain whether of extension or rotation puts the wire in a state to flow viscously" (under tension). In order to see if the highly-twisted wire commences to flow viscously at a rate that would affect the elongation sensibly, a soft drawn copper wire of diameter 0.0375 cm. was loaded to 1.020 kg. per sq. cm. and twisted to 2.5 turns over cm. (nearly to its breaking-point). The extension produced by this twist was 6.45 per cent., whereas the subsequent extension observed under this tension without further twisting was only 0.01 per cent. after 1 hour and less than 0.02 per cent. after a further 12 hours.

Experiments were also made to ascertain whether within the range of rates of twist employed the elongation is a function of the *rate* of twisting. Some of the results obtained are given in Table IV. (using the notation of the previous tables).

TABLE IV.

Twist—Elongation Measurements for different
Rates of twisting.

$L=780$ grams, $t=195$ kg. per sq. cm., $D=0.0715$ cm.

Length of wire 1.75 metres.

Rate of twisting (turns per cm. per second).	0.038	0.0038	0.00038
T.	e.	e.	e.
1	1.06	1.10	0.98
2	1.97	2.00	1.89
3	2.86	2.90	2.76
4	3.80	3.84	3.65
4.9.....	4.64	4.69	4.47

These differences are barely significant.

These experiments seem to show that (at room temperatures), within the range of tension and rate of twist employed, the elongation is a function merely of the torsion and the tension applied to a given wire.

This work is being continued, and extended to include the study of twist similarly in other materials under various conditions, with, among other objects, that of ascertaining whether definite family relationships reveal themselves between metals of which the structures are known from X-ray analysis to be similar.

The experiments which initiated this work were carried out at the suggestion of W. S. Denham, D.Sc., F.I.C., Director of Research of the British Silk Research Association, to whom I am greatly indebted for helpful advice.

References.

- (1) Ercolini, *N. Cimento*, xi. p. 43 (1906).
- (2) Poynting, *Proc. Roy. Soc. A*, lxxxii. p. 546 (1909).
- (3) Poynting, *Proc. Roy. Soc. A*, lxxxvi. p. 534 (1912); or 'Collected Papers,' Cambridge University Press, 1920.
- (4) Tammann, 'Text-Book of Metallography,' p. 81. Chemical Catalogue Co., New York, 1925.
- (5) Andrade, *Proc. Roy. Soc. A*, xc. p. 336 (1914).
- (6) Beilby, *Phil. Mag.* ser. 6, vol. viii. p. 262 (1904).

LXXIX. *The Magnetic Properties of some Compounds of Manganese.* By L. F. BATES, B.Sc., Ph.D., Senior Lecturer in Physics, University College, London*.

FERROMAGNETIC materials have recently assumed great importance from the point of view of theory and of practical application, and it is desirable to have full information on all such substances which may be artificially prepared. It is intended in this paper to report further upon the properties of two simple compounds of manganese, namely a compound of manganese and phosphorus and a compound of manganese and arsenic, whose compositions may be respectively taken as MnP and MnAs to a very close degree of approximation. Experiments with the arsenic compound (Bates, *Proc. Roy. Soc.* cxvii. p. 680, 1927) have shown that it is ferromagnetic with a magnetic critical point at 45°C . It is characterized by very pronounced thermal changes in the region between 38° and 45°C . It also exhibits a temperature hysteresis, for, although it loses its ferromagnetic properties at 45°C ., these properties do not reappear until a temperature of 34°C . is reached. The phosphorus compound has been investigated by B. G. Whitmore (*Phil. Mag.* vii. p. 125, 1929). It possesses a magnetic critical point, not so sharply defined as that of the arsenide, below 40°C ., but its thermal changes are very much less pronounced and it does not exhibit a temperature hysteresis. Both substances have been prepared in the form of powders, but the arsenic compound possesses very definite crystalline characteristics.

Ferromagnetic Properties.

For the measurement of the magnetic properties of the substance in fields of various magnitudes the usual magnetometer method was employed. The substance was placed in a copper tube 22 cm. long and 0.508 cm. in diameter. The tube was fitted with copper plugs, so that the length of tube occupied by the magnetic specimen was 20 cm. Brass rods could be attached to these plugs, so that the specimen could readily be mounted axially in a

* Communicated by Prof. E. N. da C. Andrade.

vertical water-cooled solenoid. In order to facilitate the maintenance of a steady temperature around the specimen, a glass tube 3.5 cm. in diameter was mounted inside the solenoid. Guide rings were provided so that the specimen could be accurately placed in position at any time. The solenoid consisted of eight layers of No. 18 S.W.G. double cotton-covered wire; its internal diameter was 4.15 cm., its external diameter 5.99 cm., and in all 2415 turns were wound on a length of 40 cm. The field acting on the specimen was calculated from the formula given by Adelsberger (*Ann. der. Phys.* lxxxiii. p. 186, 1927).

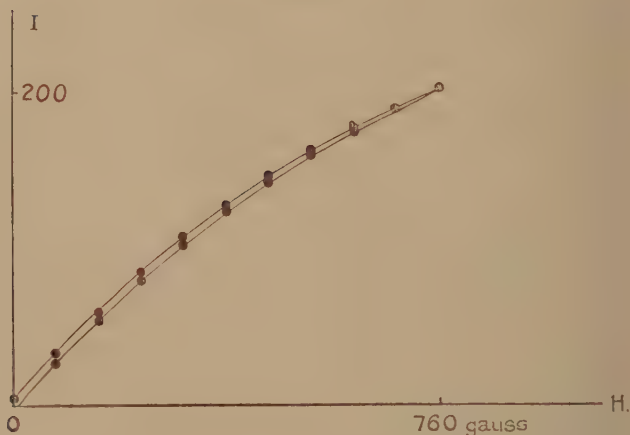
The magnetometer was adapted from an excellently made piece of apparatus designed by Carey Foster for his projected determination of the standard ohm. It was provided with two vertical coils each of 20 layers of 20 turns per layer, the mean radius of the inner layer being 17.58 cm., the mean radius of the outer layer 18.91 cm., and the centres of the coils 18.28 cm. apart. The magnetic system and mirror were suspended by a fine silk fibre. The whole possessed considerable moment of inertia to counteract the effects of small stray fields of a temporary nature. The effect of the field of the solenoid on the system was neutralized by the suitable adjustment of three circular coils wound with the same wire as, and in series with, the solenoid. Two of the coils were about a foot in diameter, and the other 4 inches in diameter. On placing a demagnetized specimen in the solenoid, the magnetizing current was switched on and the resulting magnetometer deflexion was immediately neutralized by sending an appropriate current through the magnetometer coils. This current was measured on a calibrated millivoltmeter shunted by a suitable resistance. With practice, a complete series of measurements could be taken very quickly without appreciable heating of the solenoid, even when a maximum current of 10 amperes was used.

Fig. 1 shows one-half of a typical hysteresis cycle obtained with a specimen of the arsenide when surrounded by melting ice. It will be observed that even with a field strength of 760 gauss, saturation is by no means attained. In this experiment the powder was tightly packed, so that the density of the packing was 3.68 gm. per c.c. The maximum value of the intensity of magnetization attained was 203.2 c.g.s. units. Hence the value of the maximum magnetic moment per gm. of arsenide in this experiment

was 55.1 units. Hysteresis curves were also obtained when the specimen was at room temperature and when at the temperature of liquid air, the latter condition being obtained by mounting the specimen inside an elongated Dewar flask, containing liquid air, placed inside the solenoid. In the latter case the magnetization for the same maximum field was increased to 220.2 units, the curve being of almost identical shape, with a trifle less hysteresis.

The magnetic properties of the phosphide were not so pronounced as those of the arsenide; the hysteresis was

Fig. 1.



very small, and, as shown in fig. 2, the maximum intensity of magnetization for a field of 760 gauss and a packing of 2.24 gm. per c.c. was 24.0 c.g.s. units; *i. e.* under these conditions the maximum magnetic moment was 10.7 units per gm.

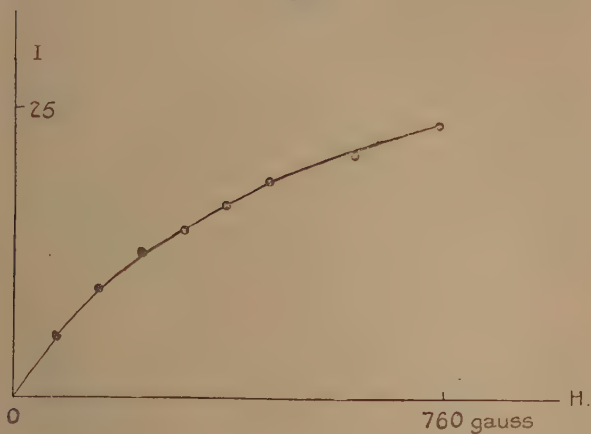
Properties above the Critical Temperature.

All previous work on the magnetic properties of these compounds has been confined to temperatures below or only slightly above the magnetic critical point. Above this point the compounds are strongly paramagnetic, and

a preliminary investigation, kindly carried out for me by Mr. B. G. Whitmore, showed that the chemical balance method would be the most satisfactory with the apparatus at our disposal. The arrangement of the apparatus is shown in fig. 3.

An outer copper vessel of the shape depicted in section in fig. 3 was placed with the lower portion between the poles of a Du Bois electromagnet, whose circular pole pieces were 8 cm. in diameter. The diagram is approximately drawn to scale, the vessel being 7 cm. wide and 12 cm. long. It was suitably lagged with cotton-wool and

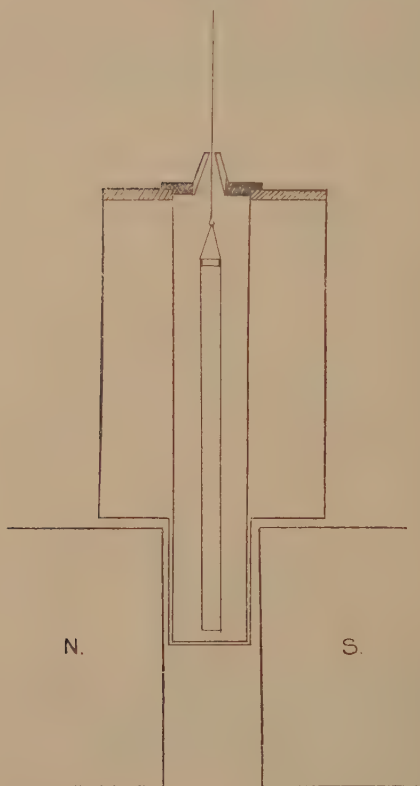
Fig. 2.



cardboard, and provided with a wooden cover. A rectangular copper tube, soldered in a vertical position in the middle of the vessel, provided a chamber in which the specimen could be suspended. The material was packed inside a uniform copper tube, the lower end of the tube being closed by a thin copper disk, and the upper end by a small copper plug. Copper has obvious disadvantages for such work, but it was felt that uniformity of temperature and easy passage of heat were so important that copper was used. Preliminary experiments showed that the magnetic effect of the copper tube in air was quite negligible compared with the magnetic effect of the material it

contained at all temperatures at which measurements were made. To the upper end of the tube was soldered a loop of copper wire with a stiff wire ending in a hook so that it could be attached to the lower end of a long

Fig. 3.



straight brass wire suspended from one arm of a sensitive balance. The hooked wire passed through a soapstone guide, consisting of a suitably bored gas-burner fitting, mounted in a cork plug fitted to the top of the copper chamber. When powerful magnetic fields were used, there was some tendency of the specimen to lateral motion,

and the guide served occasionally to maintain it in its undisplaced position with a minimum of frictional resistance to vertical motion. The outer vessel was filled with B.P. paraffin, which was electrically heated and very efficiently stirred with a centrifugal stirrer. The temperature was measured by a mercury thermometer, placed inside the chamber with its bulb close to the lower end of the specimen. For purposes of temperature control a similar thermometer was placed in the oil. The copper vessel of fig. 3 was used only for measurements up to 163° C. For higher temperatures an electric furnace was used; it consisted of a copper tube 15 cm. high, whose internal and external diameters were 2.5 and 4.5 cm. respectively. The temperature was measured as before and could easily be kept constant to 0.1° C.

We have seen that it was not necessary to apply a correction for the magnetic effects of the copper tube. Experiment also showed that the magnetic effect of the air displaced by the specimen might also be neglected. Hence, as the substance is paramagnetic, on exciting the electromagnet so that a field H is established at the lower end of the specimen and a very much weaker field H_0 at the upper end of the specimen, the specimen experiences a downward force given by

$$W = \frac{1}{2} \cdot K \cdot \alpha \cdot (H^2 - H_0^2),$$

where K is the susceptibility per c.c. of material, and α the area of cross-section of the specimen. For our purposes it is more satisfactory to express the force in terms of the susceptibility per gm. of the substance. If, then, there are m gm. of the substance in 1 c.c. and the length of the tube occupied by the substance is l , we may write

$$W = \frac{1}{2} \cdot K \cdot \frac{m \cdot \alpha \cdot l}{m \cdot l} (H^2 - H_0^2) = \frac{1}{2} \cdot K_m \cdot \frac{M}{l} \cdot (H^2 - H_0^2),$$

where K_m is the susceptibility per gm. and M is the total mass of the substance. The weights used in the determination of W were calibrated by the method of Pienkowsky (Bur. of Standards Comm. xxi. p. 65, 1916). The magnetic fields were measured by a Grassot fluxmeter, which was usually shunted so that one division on the fluxmeter scale was equivalent to a change of 38.43 lines of force per sq. cm. Corrections were, of course, applied

for the residual fields when the electromagnet was not excited.

Results for Manganese Arsenide.

In the experiments on the arsenide a copper tube of internal diameter 0.506 cm. was used, the length of tube

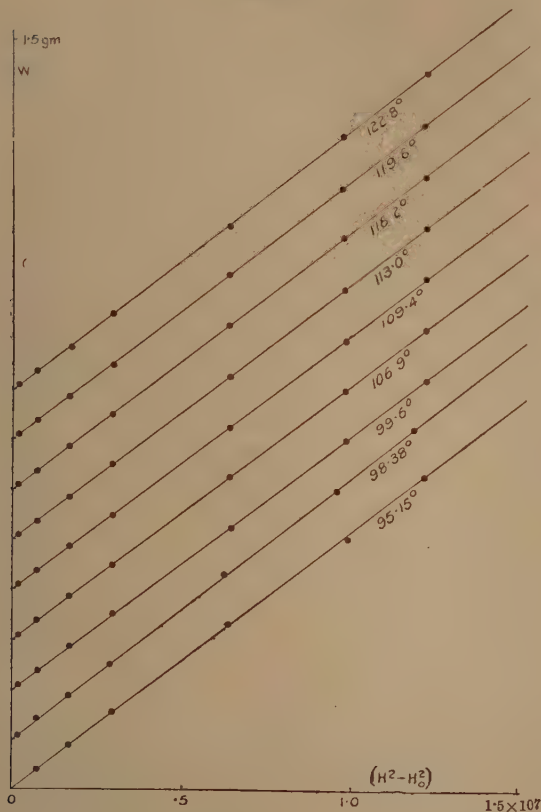
Fig. 4.



occupied by 8.535 gm. of the substance being 10.95 cm. The behaviour of the material is shown by figs. 4, 5, and 6, in which each curve represents the values of W plotted against $(H^2 - H_0^2)$ at a given temperature, *i. e.* each curve is an isothermal. It will be noted that the curves are all

concave towards the axis of $(H^2 - H_0^2)$ until a temperature in the neighbourhood of 92° C. is attained, after which all isothermals, up to the highest temperature investigated, are straight lines passing through the origin. For the sake of clearness, the isothermals in figs. 5 and 6 have been

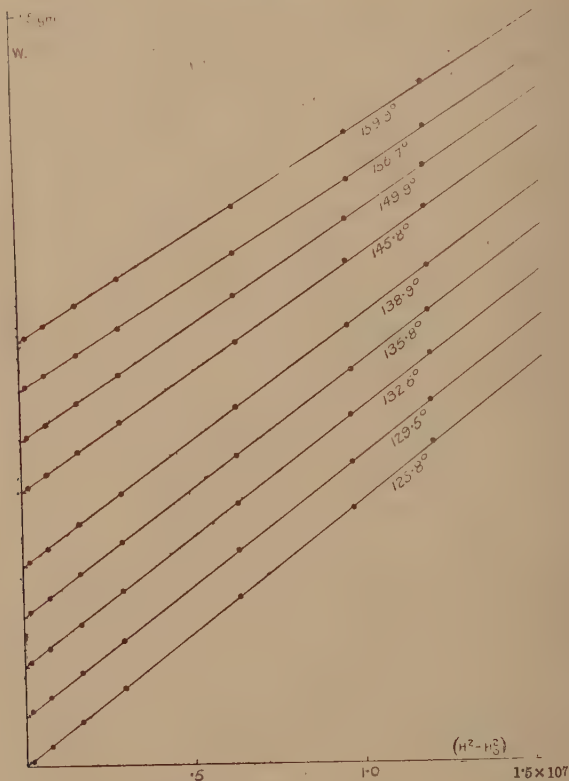
Fig. 5.



drawn with ordinates displaced upwards. It is clear from fig. 6 that a transition is occurring in the temperature region between 90° and 130° C., for here the isothermals have practically the same slope. Their behaviour is perhaps rendered more clear by reference to fig. 7, where

the force for a value of $(H^2 - H_0^2)$ equal to 1.195×10^7 units is plotted against the temperature. It will be observed that the force is practically constant over the temperature range from 92° to 130° C., and it is rather surprising that the isothermals in this region should be straight lines.

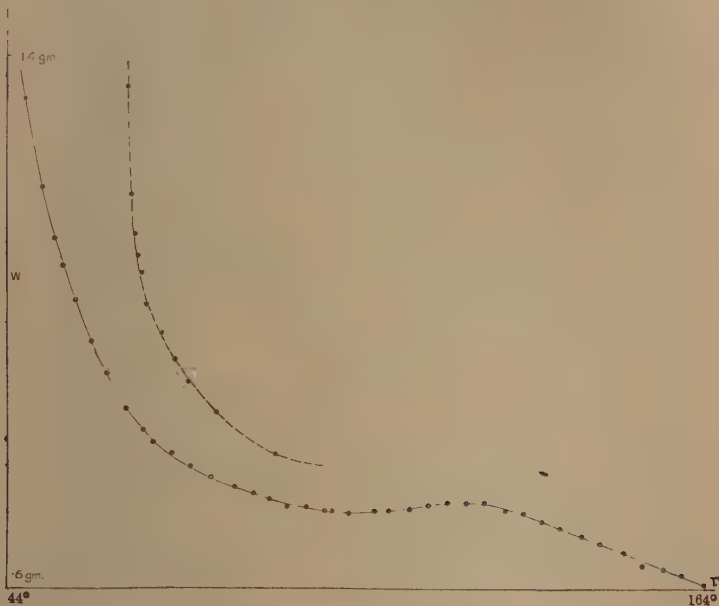
Fig. 6.



Curves similar to fig. 7 could, of course, be given for other values of $(H^2 - H_0^2)$, but no further point of interest has been noted to justify their inclusion here. It should be stated that the points plotted in fig. 7 were obtained in a definite sequence. Each point, of course, represents a value obtained from a separate isothermal. Only a few

such isothermals could be obtained on one day, and as it was thought that the preliminary experiments indicated the occurrence of some permanent change, in addition to the temperature hysteresis already described, when the substance was heated above about 70°C. , the isothermal for the temperature nearest the critical point was first obtained, after which the isothermals for successive higher

Fig. 7.



temperatures were obtained. The danger of permanent change, however, seems to have been somewhat overestimated. This is, perhaps, sufficiently clear from the orderly arrangement of the points in fig. 7, for some of the consecutive points were obtained from isothermals recorded at different times separated by intervals of some days. In addition, a series of experiments was carried out at the close of the above series of experiments to test directly for permanent changes. The specimen was heated to 55°C. and the force for a known field was obtained. It was then

heated to 100° C., cooled to room temperature and again heated to 55°, when the force was again recorded. This process was repeated several times. The first reading was always a very little greater than subsequent readings, but the latter were always the same within the limits of experimental error and on different days.

In view of the temperature hysteresis, it was considered of interest to obtain a set of isothermals for the substance when it was first heated to 100° C. and then allowed to cool to temperatures down to 34° C. Between 58° and 34° C. eleven such isothermals were obtained. They are not reproduced here, it being sufficient to mention that they showed a marked similarity to the isothermals for temperatures below 92° C., shown in fig. 4. For the sake of comparison the force is plotted against temperature for the same value of $(H^2 - H_0^2) = 1.195 \times 10^7$ units, in the broken curve of fig. 7, the abscissæ of the curve being displaced by 30° for convenience in plotting. It is seen that as the point at which ferromagnetism is regained is approached, the rate of increase of the force is rather greater than the rate of decrease shown by the smooth curve of fig. 7. This is the more noteworthy as experimental error would tend to cause a reverse state of affairs.

For assistance in the discussion of results, the reciprocals of the forces shown in the initial portion of the smooth curve in fig. 7 have been plotted against temperature in fig. 8. It is clear from the isothermals and from fig. 8 that below 92° C. the substance does not possess a paramagnetic susceptibility independent of the field, and between 92° and 130° C. we have a susceptibility which is practically independent of the temperature and independent of the field. In fig. 9 are plotted the values of $1/K_m$ for temperatures between 130° and 370° C. We see that the graph is approximately a straight line. In other words, in this region the substance obeys the Weiss law, which may be written

$$K_m = \frac{M^2 \cdot z^2 \cdot \mu^2}{3 \cdot M \cdot R} \cdot \frac{1}{T - \theta} = \frac{C}{T - \theta},$$

where M is the molecular weight of the substance, μ the magnetic moment per molecule, θ a temperature characteristic of the material, R the gas constant, and T the absolute temperature. This may be rewritten

$$M \cdot z \cdot \mu = \sqrt{3 \cdot M \cdot R \cdot K_m} \sqrt{T - \theta}.$$

Fig. 8.

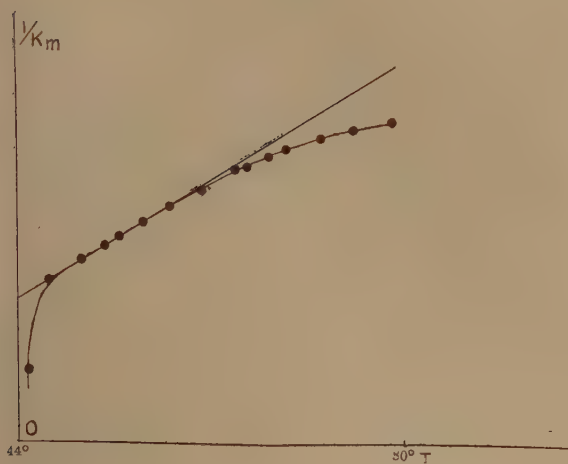
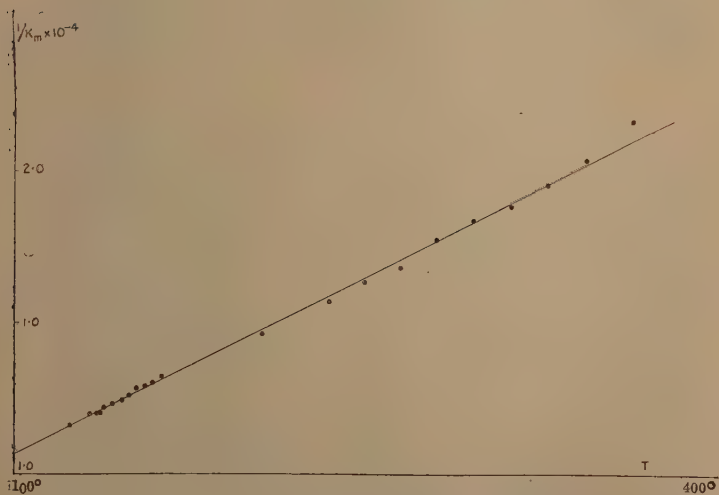


Fig 9.



From fig. 9, θ was found to be 274.5° abs., and the value of K_m at 636° abs. was taken as 4.675×10^{-5} c.g.s. unit per gm., whence $M \cdot z \cdot \mu = 2.34 \times 10^4$ c.g.s. units or 20.83 Weiss magnetons, or 4.2 Bohr magnetons, per gm. mol.

A tangent was also drawn as shown in fig. 8, and θ here was found to be 294.1° abs. and $M \cdot z \cdot \mu$ was 3.87 Bohr magnetons per gm. mol. Of course these particular values are unreliable, and are only included here for the sake of completeness. It is interesting that the two results for $M \cdot z \cdot \mu$ are so close. We are singularly reminded of the behaviour of Fe β and Fe δ , which have the same structure, but it would be unwise to attach too much importance to this resemblance.

It now remains to calculate the value of the factor ν by which the intensity of magnetization of the specimen must be multiplied in order to obtain the value of the Weiss internal field. This may be obtained from the expression $C = \theta / \nu \rho$, where C and θ have the same meanings as before, and ρ is the density of the substance, which at room temperature is 6.02 gm. per c.c. From fig. 8 the value of ν is 3390 and from fig. 9, 2700. It must be emphasized that we have used the value of the density at room temperature in both calculations, so that the results, particularly the second, must be regarded as approximate only. Their order of magnitude is, however, quite in accord with the values of ν obtained for other ferromagnetic substances.

Results for Manganese Phosphide.

In the experiments on the phosphide a similar copper tube was used, the length of the tube occupied by 5.884 gm. of the powder being 11.7 cm. Once again the preliminary experiments showed the magnetic effect of the copper tube to be negligible, and again the magnetic effect of the air could be neglected. Isothermals up to 140° C. were obtained with the apparatus of fig. 3, and up to 265° C. with the electric furnace. The isothermals for 36.1° C. and for all higher temperatures were straight lines, within the limits of experimental error, and the isothermals for 31.95° and for 34.05° C. were not very markedly curved. There was no sign of permanent change or of temperature hysteresis. Fig. 10 shows some of these isothermals.

Fig. 11 shows the behaviour of the reciprocal of the susceptibility with temperature. There appears to be a

slight discontinuity about 135° C., but it is doubtful if it has any real significance, for, as we have seen, the experimental arrangements were completely changed at this juncture and the magnetic field completely altered, so that

Fig. 10.



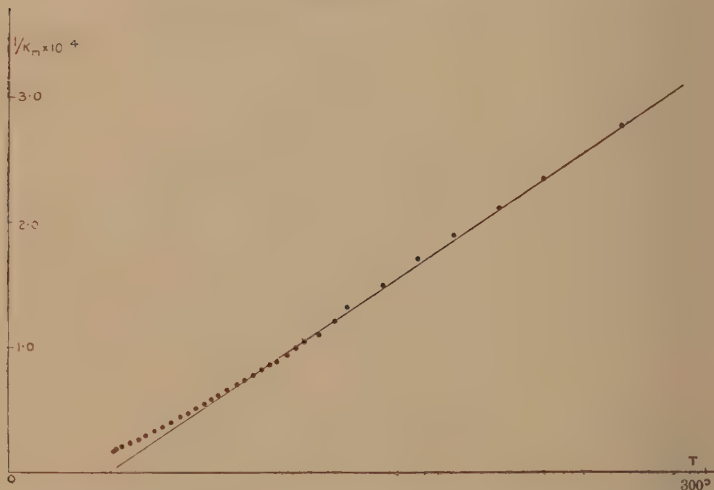
there is a distinct possibility that a slight discontinuity may enter into the work here. From fig. 11 it was found that for $(H^2 - H_0^2) = 1.477 \times 10^7$ units the downward force when the temperature was 300° C. was 0.1188 gm., and θ was found to be 42° C. Hence, at 300° , $K_m = 3.137 \times 10^{-5}$ c.g.s.

unit, so that $M. z. \mu$ is equal to 11.83 Weiss magnetons or 3.69 Bohr magnetons per gm. mol. The factor ν for the Weiss internal field is found to be 8080, the density of the substance at room temperature being 4.82 gm. per c.c. The value of the factor is in good accord with the values for the arsenide, when the properties of the two substances are remembered.

Discussion of Results.

A considerable amount of attention has recently been paid to the theoretical aspect of ferromagnetism; in

Fig. 11.



particular, a theory based on the conceptions of wave mechanics has been advanced by Heisenberg (*Zeit. f. Phys.* xlix. p. 619, 1928). This theory has been discussed by Fowler and Kapitza (*Proc. Roy. Soc.* cxxiv. p. 1, 1929) and extended to account for magnetostriction and the large changes in specific heat which occur at the magnetic critical point. Fowler and Kapitza show that if a ferromagnetic substance contains one magnetizable electron per atom, then the theory requires a "step-down" in the value of the specific heat at constant volume by an amount approximately equal to a little less than 3 calories per gm. mol. as the temperature rises through the magnetic critical

point from below. In support of this view they quote the results for nickel obtained by Weiss and his collaborators. The more recent and more accurate results of Potter and Sucksmith (Proc. Roy. Soc. cxii. p. 157, 1926) also support the conclusions, viz. that the results for nickel fit the theory. The available data for iron and magnetite, however, do not fit, and it is therefore concluded that for these substances a theory based on the presence of two or three magnetizable electrons per atom is required. Such a theory has not been worked out, but Fowler and Kapitza consider that it would differ only from that already given in complication of detail, and would give a "step-down" in specific heat respectively two or three times as great as that given in the single electron theory, and thus be in agreement with the experimental values. This generalization, however, cannot always be permissible, for the writer has shown (Bates, *loc. cit.*) that 1 gm. of the arsenide requires 1.79 calories to enable it to change from the ferromagnetic state at 36° C. to the paramagnetic state at 45° C. The so-called "step-down" in the specific heat at the magnetic critical point is roughly 0.9 cal. per deg. per gm., or 120 cal. per deg. per gm. mol. If the above generalization is correct, the number of magnetizable electrons must be of the order of 40 per molecule, which is very unlikely. Of course the huge heat changes may be brought about by a change in lattice structure, and here the results of an X-ray examination will be of interest. The experimental evidence above the magnetic critical point indicates that 4 Bohr magnetons and not 40 are associated with 1 gm. mol.

When we try to picture the processes which are here in operation, we have to remember that we must explain the disappearance of ferromagnetism at 45° C., the very slight variation of magnetic susceptibility with temperature between 92° and 130° C., and the very pronounced temperature hysteresis. We ought, perhaps, to treat the hysteresis phenomena in two portions, but this seems scarcely necessary in a preliminary discussion without the benefit of X-ray analysis. We may imagine that ferromagnetism arises through the association of atoms in groups as outlined by Stoner, or as a regular distortion of the crystal lattice as viewed by Derflinger and Ewald, or through the forces between electrons which are described as homopolar valency forces by Heitler and London. At the magnetic

critical point the groupings, or distortions, and the forces disappear. The crystal remains intact, of course, because these forces are only a fraction of the total forces which hold the crystal together. It follows that the elastic constants of the crystal should change as one passes through the magnetic critical point, and steps will be taken to investigate this with the arsenide. In the case of the arsenide it is clear that the groupings and the forces are not always re-established when the initial temperature conditions are restored. This means that at least two stable groupings are possible, or that the disappearance of ferromagnetism is accompanied by a change in position of some constituent of the crystal which has two or more stable positions of equilibrium. Now, in the case under discussion, we have, comparatively speaking, tremendous changes, between 36° and 45° C., but above 45° C. the magnitude of the specific heat does not excite comment. Hence any change in grouping is probably almost complete at 45° C., and further changes are likely to be only slight. However, these slight changes are accompanied by hysteresis phenomena. It is suggested here that these are due to the disturbing effects produced by loosely bound particles, each of which may occupy several positions of equilibrium. Let us consider two regularly formed crystal layers of atoms separated by certain loosely bound particles which constitute a crystal boundary, a conception which is based upon that given by Prandtl in his explanation of elasticity hysteresis. We may further consider that these particles themselves contribute little or nothing to the magnetic moment of the specimen, but they are entirely responsible for the occurrence of hysteresis. The loosely bound particles may be taken to come into play when the substance is passing through the magnetic critical point. From the evidence of hysteresis curves taken when the maximum temperature to which the specimen is heated is higher or slightly lower than the critical temperature, it is clear that several equilibrium positions of the loosely bound particles must be possible. When the ferromagnetic groupings have broken down, the loosely bound particles take up positions of great stability, so that the reconstruction of the groupings on cooling is impossible, until conditions are such that the particles are able to move to positions of lower potential energy, where they cannot affect the reconstruction of the groups. This is sufficient

to explain the hysteresis phenomena observed when we heat the substance to slightly over 45° C., and, clearly, little difficulty lies in the way of the extension of this idea to explain the hysteresis phenomena at higher temperatures, for there appears to be no difficulty in the way of extending the number of positions of equilibrium.

The behaviour of the substance between 92° and 130° C., however, calls for further comment. The susceptibility over this range of temperature may be regarded as approximately constant, and we are led to compare its behaviour with that of potassium bichromate in the solid form and in solution (*cf.* Weiss and Mlle Collet, *Comp. Rend.* clxxviii. p. 2146, 1924; and clxxxi. p. 1057, 1925), and of solutions of luteocobaltic chloride. To explain the constancy of these paramagnetic susceptibilities with temperature, Weiss has suggested that in these cases the resultant magnetic moments of all the electron orbits in the molecules are zero, and that constant magnetic susceptibility is due to an orientation of some kind in which only a portion of an atom is involved, and must therefore be regarded as an intra-atomic phenomenon. If we may extend this argument to manganese arsenide, then presumably an internal electron arrangement in the manganese atom would be responsible for the constant paramagnetism. The presence of loosely bound particles places no difficulties in the way of the Weiss explanation.

It remains to consider what constitutes the above-mentioned loosely bound particles. A possible conjecture is that they are atoms of arsenic. The mode of formation of the substance would certainly appear to lend itself to the production of such loosely bound particles of arsenic, which should themselves neither contribute to the magnetic susceptibility nor give rise to appreciable temperature variations.

When we consider the results for manganese phosphide, we have the results of Whitmore (*loc. cit.*), which show that there is no very pronounced change in specific heat at the critical point. We should have expected, according to Fowler and Kapitza's arguments, a much greater change of specific heat, although it may be urged that only one atom in each ferromagnetic grouping possesses a resultant magnetic moment. Since 3.69 Bohr magnetons per gm. mol. are associated with the phosphide, we may perhaps consider that only about one in every two manganese

atoms contributes to the magnetic moment. Even this, however, would require a much more pronounced change of specific heat than is actually observed. The behaviour of the isothermals below 40° C. at first occasioned some surprise, but actually the fact that the isothermals are straight lines before this temperature is reached really means that the magnetic critical point is well below that temperature. Whitmore's curve of magnetic induction with temperature shows that $I.dI/dT$ is a maximum at 17° C., and the ferromagnetic properties must disappear below 30° C. We are, in fact, dealing with a very weakly ferromagnetic substance which becomes very strongly paramagnetic above the magnetic critical point, and the curve of magnetic induction with temperature, for a given field, is liable to misinterpretation.

Further experiments with these substances are contemplated and are already in hand. Firstly, a complete X-ray examination over a wide range of temperature is to be carried out. Secondly, steps will be taken to obtain a large single crystal of the arsenide, to test its directional properties and the variation of the elastic constants in the neighbourhood of the magnetic critical point.

Summary.

Observations have been made of the magnetic properties of two simple compounds of manganese, a phosphide and an arsenide, at temperatures above their magnetic critical points, where both substances are strongly paramagnetic. In the case of the arsenide the susceptibility is practically constant over a range of temperature from 90° to 130° C., after which the Weiss law is obeyed. The nature of the temperature hysteresis which this substance exhibits is discussed, and an explanation based on the presence of loosely bound particles of arsenic is put forward. In the case of the phosphide the Weiss law is approximately obeyed.

The writer has already acknowledged his indebtedness to Mr. B. G. Whitmore for assistance in the early stages of the work. It remains for him to express his deep appreciation of the kind and helpful interest which Professor E. N. da C. Andrade has taken in these experiments.

Carey Foster Laboratory,
University College, London.

LXXX. *Some Factors governing the Magnitude of Frictional Electric Charges.* By P. A. MAINSTONE, M.Sc., Lecturer in Physics in the University College of North Wales*.

IN recent measurements of frictional electricity attempts have been made to control the actual conditions of rubbing, and to reduce the number of unknown factors to a minimum.

Shaw¹ established a frictional series, and investigated the effects of temperature variation, flexure of the rubbing surfaces, changes in the mechanical nature of the surfaces, etc. The effect of the surrounding medium must clearly be an important factor, and the first investigation of this nature was made by J. H. Jones², who measured the maximum charge produced on a given specimen in various gaseous and liquid media. He found that in the case of gaseous media the charge generated in air was greater than in any other gas except sulphur dioxide. It appears doubtful, however, whether the gases used in these experiments were entirely free from moisture, and the action of moisture in reducing the magnitude of frictional charges is well known. Vieweg³ drew up a frictional series including a number of crystalline substances and discussed the order of various elementary substances in the series. When two surfaces are rubbed together, that surface whose atoms or molecules give up electrons more readily becomes positively charged with respect to the other. Thus atoms with low ionization potentials should lie at the positive end of the series, those with high potentials at the negative end. Several metals included in the series conformed to this order. Vieweg also made an exhaustive examination of the effect of water vapour, and found that it produced an additional positive charge on each of the rubbing surfaces. A surface normally negative had its charge reduced when moisture was present, and if the normal charge was small, its sign might even be reversed. This effect might explain some of the apparent anomalies often observed. Macky⁽⁴⁾, using various insulators rubbing on polished metal surfaces, examined the effect of the surrounding medium, and was the first to observe the effect of varying the gas pressure. The charge

* Communicated by Prof. E. A. Owen, M.A., D.Sc.

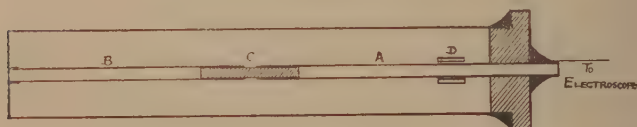
generated by a given rubbing process diminished as the pressure was reduced until at a pressure of 1 or 2 mm. it had dropped almost to zero. This effect was observed in all the gases used, but no appreciable differences between the magnitudes of the charges in the different gases was noted.

The present research was undertaken with a view to measuring the frictional charges produced by a very small amount of mechanical work, and also to investigate the effect of the surrounding medium.

Apparatus.

The first apparatus used consisted of a brass tube about 45 cm. in length and 5 cm. in diameter, along the axis of

Fig. 1.



- A. INSULATED RAIL.
- B. EARTHED RAIL
- C. EBONITE BRIDGE.
- D. SLIDING RUBBER.

which was fixed either a circular brass rod or a narrow flanged brass strip. The rod or strip was divided into two portions which were bridged by ebonite, one portion being insulated while the other was earthed. Fig. 1 makes the arrangement clear. The tube was arranged to tilt about a horizontal axis at one end so that a rubbing substance could move under gravity along the central rod or strip. A silk-wound bobbin was used in one case, and a small piece of plate glass in the other. The arrangement of the tilting tube was such that the insulated portion of the insulated rod lay uppermost, and this was connected to the measuring electroscope. Starting with the rubber at the end of the insulated portion (see fig. 1), both being at zero potential, and the tube horizontal, sufficient tilt was given to the tube for the rubber to slide down with as little acceleration as possible. When the rubber passed over

from the insulated to the earthed portion of the rod, a deflexion of the electroscope was observed. Contact with the earthed rod was found sufficient to discharge the rubber, and no ionizing agent was necessary.

The tilting tube was connected by rubber pressure tubing or a horizontal glass taper joint to the usual vacuum apparatus. Gas pressures from atmospheric pressure down to about 1 cm. were read by a vertical mercury column, and lower pressures by a McLeod gauge. A hand-worked oil pump served to evacuate down to about 1 mm., and lower pressures were obtained by the use of charcoal and liquid air.

Considerable potentials were developed even when the amount of mechanical work was made extremely small. The mass of the rubber was reduced to a few grammes, and the length of the insulated rod to a few centimetres. The potentials, which were measured on a quadrant electrometer, were generally of the order of 10 to 20 volts.

The effect of water vapour in the apparatus was always very pronounced. Brass, when rubbed by either silk or glass, acquires a negative charge, but the magnitude of the charge increases considerably when the surrounding atmosphere is made perfectly dry. In the present experiments the apparatus always contained phosphorus pentoxide, and the contained gas was always left for a sufficient time for all water vapour to be completely absorbed.

The charge per single rub was generally found to increase with the number of previous rubs until a steady value was reached. This effect has been observed by most other experimenters, and is considered by some to be due to a surface flow of molecules in the rubbed specimens. From the present measurements, however, it would appear probable that the effect is largely due to adsorbed gas films on the rubbing surfaces. This point will be referred to again later.

The effect of varying the gas pressure was not very marked, or was probably masked by other spurious effects. There were indications, however, of a reduction of charge at pressures of a few millimetres, with a subsequent increase at very low pressures.

The brass rod used in these measurements was rubbed with fine glass or emery paper before being fixed in position. The silk-wound bobbin was cleaned in a boiling

solution of powdered soap and common soda, well washed, and dried. On removal from the apparatus after measurements had been made, the silk was always found to be considerably soiled. Such rubbing surfaces are clearly very indefinite. The preparation of a metal surface by distillation *in vacuo* would be a marked improvement in the measurement, but in the present experiments the practical difficulties are considerable. In Macky's work small hand-polished surfaces, approximately plane, were used, and on the publication of this work the apparatus was modified to make the use of polished surfaces possible, while still employing the principle of moving the rubber from an insulated to an earthed surface.

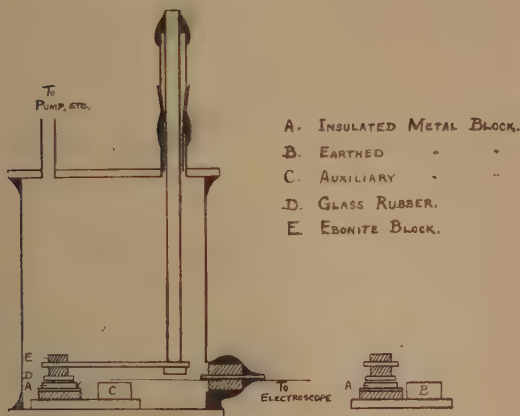
The new friction chamber consisted of a brass cylinder 10 cm. in length and 8 cm. in diameter. This was closed at the ends by overlapping brass disks, and the joints were rendered airtight by picein wax.

The first metal used was brass. Three short lengths were cut from rod 1.8 cm. in diameter. Two were turned down to equal length, while the third was made somewhat shorter, the difference corresponding to the thickness of a small ebonite block on which this particular specimen was intended to rest. When the two longer specimens were fixed directly to a flat metal surface, while the shorter stood on its insulating block which in turn rested on the same flat surface, the upper surfaces of the three specimens could be rubbed down together on emery paper, and then polished accurately in one plane.

The arrangement of the three specimens in the friction chamber is shown in fig. 2, in which two sections at right angles are given. The shorter specimen A and a longer one B were mounted in this way as close together as possible, so that the rubber, usually a glass disk, could move across from one to the other without jolt. The third specimen C was used merely to render easier the polishing process, and played no part in the measurement of charge. In the first measurements the three specimens rested on the base of the chamber itself, B and C being always earthed, while A was insulated and connected to the measuring electroscope. In later measurements, however, the specimens were mounted on a small brass base which rested in a fixed position on the base of the chamber, and which could be removed through a window without opening the entire chamber.

The rubber consisted of a small glass disk of good optical quality. Above this was attached by wax a small block of ebonite. This enabled the rubber to be moved across from A to B by a metal arm operated from outside the chamber by the use of a glass taper joint. Fig. 2 makes the arrangement clear. The amount of travel of the rubber was made definite by attaching to the upper (male) portion of the taper joint a horizontal arm moving between fixed stops. These were arranged so that the rubber moved from a symmetrical position on the specimen A to a corresponding position on B. The distance of

Fig. 2.



travel was thus about 2 cm. The mass of the entire rubber was 2.5 grams.

The charge was measured on a gold-leaf electroscope used with the leaf system insulated and a potential of about 100 volts on the case. The sensitivity was 1.4 eyepiece divisions per volt. It was generally found necessary to increase the capacity of the apparatus in order to restrict the potentials to suitable values. This was done by the use of cylindrical air condensers. In the case of glass rubbing on metals a total capacity of about 300 cm. restricted the maximum potentials to about 20 or 30 volts.

Results.

The procedure in all the measurements was to fill the apparatus with air or other gas almost to atmospheric pressure, leaving it to dry for a period preferably of several hours. The pressure was then reduced in stages, measurements of the charge per single rub being made at each stage.

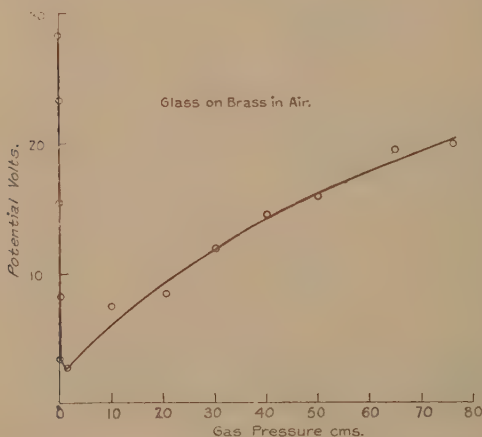
The following rubbing substances and gases were used:—

Glass on brass, steel, and silver, each combination in air, hydrogen and nitrogen.

Glass on silver in oxygen.

Ebonite on steel in air.

Fig. 3.



The metal surfaces were polished in the usual way, rouge being used for steel, and diamantine for brass and silver.

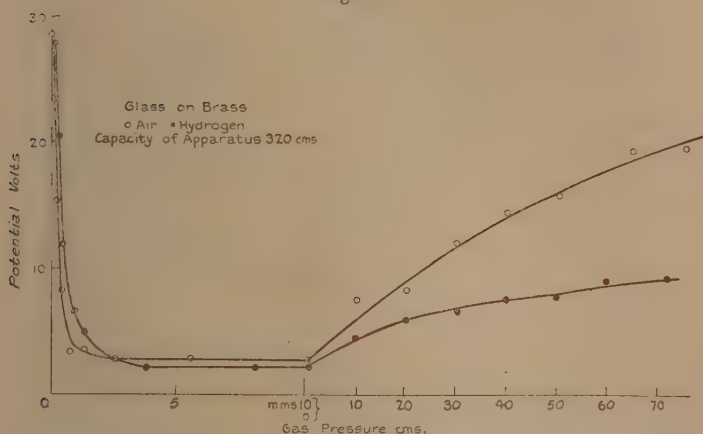
Hydrogen was generated by electrolysis, and passed directly into the apparatus. Oxygen was formed by heating potassium chlorate and manganese dioxide and nitrogen was obtained from a commercial cylinder.

The first results for glass on brass in air are shown in fig. 3. As the pressure is reduced a slight decrease in charge is apparent, the decrease becoming more rapid as the pressures approach a value of a few millimetres. A further reduction of pressure maintains a more or less

steady value of the charge, but at a pressure of about 1 mm. a rapid rise commences, and continues to the lowest pressure reached (less than 0.01 mm. as a rule). The slope of the curve in this region is too steep to be shown by the scale of pressures chosen. The same curve, however, as well as a similar one for hydrogen, is shown in fig. 3a, where the scale is chosen to show the whole range in centimetres, and also the lowest pressures in millimetres.

In many cases the value of the charge per single rub at a given pressure was quite steady, apart from the initial effect already referred to. At very low pressures, however, the values were less consistent. On reducing the pressure,

Fig. 3a.



the first rub gave in general a charge which disagreed with those given by subsequent rubs. The usual procedure was to determine the charge per rub after 10, 20, 30, etc., previous to-and-fro rubs had been given. When three or four such readings agreed, the value was taken as definite, but when gradual or irregular changes existed, the rubbing was continued until sufficient values had been obtained for a reasonable average to be accepted. This method sometimes entailed as many as 200 or 250 rubs.

It will be noted that at the higher pressures the charge developed in air is greater than in hydrogen, while at very low pressures it is less. The first effect was obtained in all the cases investigated, but the second was not always apparent.

Other results, each involving the same glass rubber, are shown in figs. 4, 5, and 6. In fig. 4 the brass specimen was

Fig. 4.

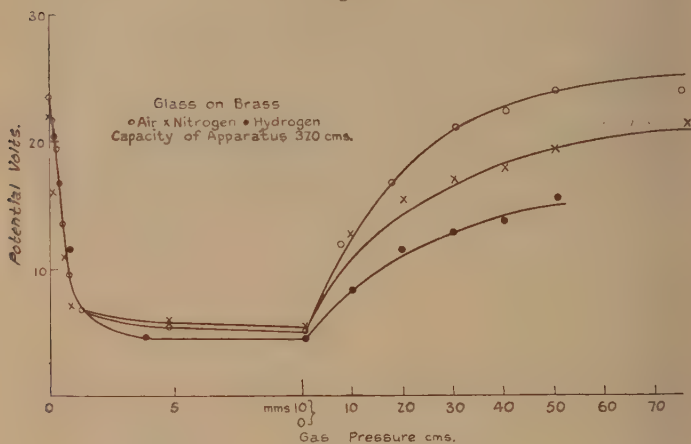
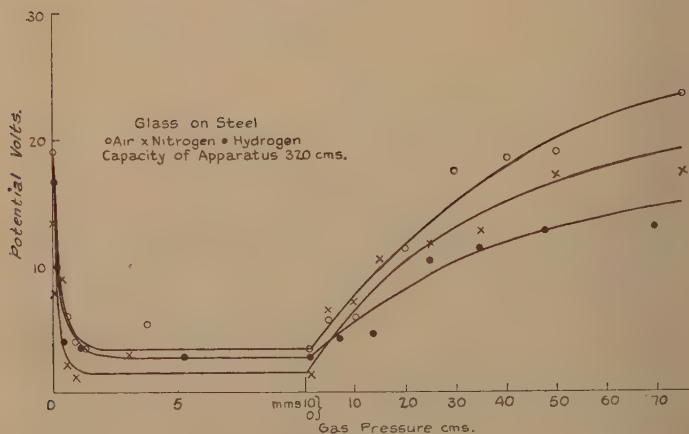


Fig. 5.



the same as in fig. 3a, but an interval of several weeks elapsed between the two sets of measurements, during which an accidental contamination of the metal occurred, re-polishing being subsequently necessary. It will be noted

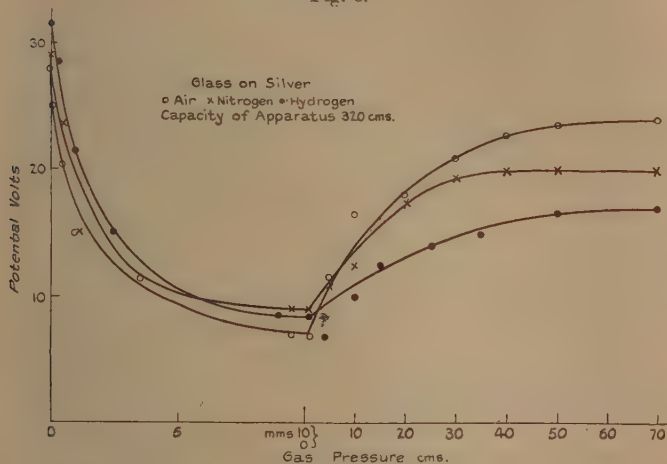
that in the second series of measurements no difference between the effects of air and hydrogen at very low pressures was apparent.

The general results of these measurements are :—

(1) At the higher pressures the charges for each of the three metals are greatest in air and least in hydrogen.

(2) At these pressures no appreciable difference exists between the charges on the three metals in a given gas at a given pressure.

Fig. 6.



(3) At very low pressures the charges on a given metal are approximately the same in each gas. At the lowest pressure reached the charge varied with the metal, being greatest for silver and least for steel. (The diameters of the silver and steel specimens were, however, slightly less than that of the brass.)

(4) The relative drop in charge at the intermediate pressures was most pronounced in the case of steel, and least pronounced in the case of silver.

Anomalous Results with Silver.

The variation of the charge per single rub with the number of previous rubs has already been referred to. For silver it was found in many cases that the charge per

rub showed a gradual increase up to a point when a sudden decrease was observed. The lower value was generally from one half to three quarters of the higher. On continuing the rubbing, a gradual rise was again observed with the subsequent sudden drop. The effect was found to be liable to exist at all but the very lowest pressures. It would appear to be due to the gradual formation of an adsorbed gas film which at a certain point was wholly or in part removed by the repeated rubbing. Wherever the effect existed, the mean of the highest and lowest potentials was recorded.

Oxygen was used only in the case of glass on silver. It was found necessary to separate the evacuated chamber from the rest of the vacuum apparatus by a closed tap until the oxygen was perfectly dry. The first readings obtained showed no appreciable difference from those in air. At this stage, however, a marked decrease in the charges became apparent. The silver specimens were removed for examination, but no appreciable tarnish of the surfaces was found. As the effect persisted, it appeared probable that it was due to the action of mercury vapour on the polished surfaces. The charges in air were hence measured from day to day. A progressive decrease in the normal negative charge was observed, the sign of the charge ultimately being reversed. This effect persisted after a temporary return to normal conditions when the surfaces were re-polished.

In order to eliminate mercury vapour from the apparatus a Pirani gauge was used to measure the pressures. This gauge⁽⁵⁾ consists of a tungsten filament which is heated by an electric current to a temperature somewhat higher than that of the surroundings. Cooling by conduction and convection varies with the gas pressure, and the heating current necessary to maintain a given temperature, and hence also a given resistance, determines the value of the pressure. The filament is included in a Wheatstone bridge with three other resistances with very low temperature coefficients, and the gas pressure is expressed in terms of the potential which must be applied to the ends of the bridge in order to maintain a balance. The gauge is primarily intended for use at very low pressures, but it was found quite easy to use at pressures up to a few millimetres. It was calibrated by means of a McLeod gauge before the latter was shut off from the apparatus. Before

measurements of frictional charges were commenced the apparatus was evacuated and re-opened to air several times in order to sweep out the remaining mercury vapour.

With this modification the silver surfaces were re-polished after a considerable layer had been removed from each. The charge in air at atmospheric pressure was first measured, after which the air was exhausted directly to a pressure of a few millimetres as given by the Pirani gauge. Charges at decreasing pressures down to the lowest attainable were then measured as before. The normal variation of the charge with gas pressure was again obtained. The chamber was left evacuated, and the charge observed at intervals over a period of about a fortnight. A very slight leak existed in the apparatus, and a slight decrease in charge was observed for this reason. No abnormal decrease, however, was noted.

Oxygen was then again admitted to the apparatus after thorough drying. The charge at a pressure of about $\frac{1}{2}$ atmosphere was a little greater than that at the same pressure in air. At low pressures the normal rapid increase of charge was observed, the charge at the lowest pressure being slightly greater than the corresponding charge in air. Observations at very low pressures were made over a further period of ten days, and although due to the slight leakage a rather more rapid decrease of charge than might have been expected was noted, there was no approach to a reversal of charge as in the previous case.

The observed abnormal decrease in the negative charge, with an ultimate reversal to positive charge, may thus be definitely attributed to the presence of mercury vapour.

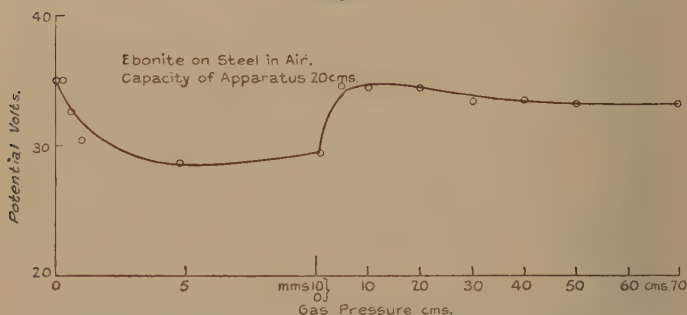
Measurements with Ebonite on Steel.

Most metals are charged negatively by glass, but steel is positive with respect to ebonite. Use was made of a small ready-to-hand ebonite disk with a moderate state of polish on its surface. The charge in air at atmospheric pressure was much less than in the case of the glass rubber, and it was found necessary to reduce the capacity of the apparatus to about 20 cm. in order to obtain potentials of the same order as before. The measurements were not very consistent on repetition, but the relative diminution in charge at the intermediate pressure was beyond doubt very much less than in the other cases dealt with. The results of one set of measurements are shown in fig. 7.

Effect of varying the Capacity of the Apparatus.

It might be supposed that the variation of charge with gas pressure could be explained by supposing conduction of the gas layer separating the two rubbing surfaces to cause partial neutralization of the two equal and opposite charges. The essential condition for this would be that the potentials generated should be sufficient to cause ionization of the gaseous molecules by collisions. Such ionization would be most efficient when the mean free path of a gaseous ion was of the same order as the thickness of the gas layer, and this condition might be expected at a pressure of a few millimetres. On this supposition the variation of charge with gas pressure should be less pronounced if the capacity of the apparatus were increased,

Fig. 7.



and hence the generated potentials diminished. The first measurements to test this point were made with the brass specimens in their original state of polish corresponding to the curves of fig. 3. The electrical capacity of the main apparatus was 176 cm., and a supplementary capacity of 146 cm. was arranged so that it could be connected to the main apparatus, giving a total capacity of 322 cm., or earthed at will. Each reading could thus be taken with two different capacities. The results are shown in Table I.

¶ Except at the very low pressures the charges measured with the two capacities are almost identical in value. At the lowest pressures the charges with the larger capacity are slightly greater than with the smaller, but the difference is not sufficiently marked to indicate any appreciable effect of varying the capacity.

In these particular measurements the maximum potentials generated with the larger capacity were still considerable, and it was thought desirable to increase the capacity of the apparatus until the maximum potentials did not exceed 1 or 2 volts. Such measurements were made for ebonite on steel and glass on steel, the gas in each case being air. Each reading was, as before, taken with the two different capacities, the higher potentials being read on the gold-leaf electroscope and the lower on a quadrant electrometer used at a sensitivity of 100 mm. per

TABLE I.
Capacity A 176 cm., B 322 cm.

Gas pressure.	Potential (Volts).		Charge (E.S. Units).	
	A.	B.	A.	B.
70 cm.	34.0	18.5	20.1	19.9
60	34.0	18.5	20.1	19.9
50	31.0	17.0	18.3	18.3
40	25.0	14.0	14.8	15.0
30	20.0	11.0	11.8	11.8
20	17.0	10.0	10.0	10.7
10	11.5	6.5	6.8	7.0
12 mm.	4.5	2.75	2.65	2.95
8	4.5	2.5	2.65	2.70
3.5	4.5	2.5	2.65	2.70
0.8	9.0	5.0	5.3	5.4
0.65	10.5	6.0	6.2	6.4
0.40	12.5	7.5	7.4	8.1
0.175	21.5	12.5	12.7	13.4
0.075	34.0	20.0	20.1	21.5
0.00	Too large to read.	25.5	—	27.4

volt. In the case of ebonite, the usual capacity of 320 cm. was sufficient to reduce the potentials to the requisite lower values, but in the case of glass, plate condensers with sulphur as dielectric were built up to a total value of about 0.01 mfd. The values of the capacities were not known with sufficient accuracy to enable the charges to be calculated, but in the following table, which relates to glass on steel, the ratio of the potentials at each gas pressure is calculated.

Similar results were obtained for ebonite on steel. If the drop in potential at the intermediate pressures is due to gaseous conduction, the effect should be more pronounced with the higher potentials, *i. e.*, with the

smaller capacity. The ratio V_B/V_A might thus be expected to diminish under these conditions. No indication of this was obtained, and it would appear that in these measurements gaseous conduction is not an important factor. There appears to be some evidence, as for example in the work of Kinsley⁶ that discharges can take place over very short distances at potentials of the order of 1 volt or less, but it cannot be said that the present experiments afford any confirmation of that result.

Discussion of Results.

If two solid surfaces entirely free from gas films or other contamination are rubbed together, the atoms or molecules

TABLE II.

Gas pressure.	Potentials (Volts).		V_B/V_A .
	V_A .	V_B .	
70 cm.	1.20	43.5	36.2
50	1.07	39.5	36.9
40	1.00	37.25	37.2
30	0.90	34.0	37.8
20	0.77	29.5	38.3
10	0.55	22.75	41.3
5	0.45	18.5	41.1
8 mm.	0.35	13.75	39.3
1.5	0.62	24.0	38.7
0.90	0.72	26.5	36.8
0.45	0.82	30.0	36.6
0.04	1.47	55.0	37.4

of each surface are subjected to disruptive influences, and an interchange of electrons between the surfaces takes place. The work required to detach an electron from the parent atom varies with the nature of the atom. Hence with two dissimilar surfaces, that surface whose atoms or molecules give up electrons the more readily becomes positively charged. Vieweg, in the paper referred to, puts forward this view, and suggests that Coehn's rule is an equivalent statement of the same fact. By this rule, substances with high dielectric constants become positively charged when rubbed with substances of lower dielectric constants, the charge being proportional to the difference between the constants for the two given substances. A substance with a high dielectric constant is one in which the binding forces on the outer orbital electrons are small,

hence such electrons could escape more readily than in the case of a substance with a lower constant.

In the present experiments, the charges generated at the lowest gas pressures, when the effect of the gas would be least, were greater for silver than for steel. The ionization potential for silver is 7.5 volts (Foote and Mohler), but reliable values for iron and silicon were not available. The relative magnitudes of the charges, however, agree with the order of glass, iron, and silver in Shaw's frictional series.

The results for pure surfaces will clearly be modified in the presence of a gas, of which the effect may be threefold :—

(1) Conduction across the gas layer separating the two surfaces may take place. This will be a small factor if either the gas pressure or the potential difference between the surfaces is very small. Its bearing on the present measurements has already been discussed, and it is considered to be relatively unimportant.

(2) Each rubbing surface will be covered by an adsorbed gas film, of which the surface density will vary with the gas pressure. The rubbing process would then tend to disrupt gaseous rather than solid molecules.

(3) The metal specimen holds a considerable amount of gas in occlusion. This gas may be assumed to be strongly ionized, and a contact potential between the occluded and the free gaseous ions would be set up due to a difference in concentration. Further the amount of occluded gas is not appreciably reduced on reducing the outside pressure, whilst the number of free gaseous ions is small, whatever the pressure. Hence this factor should depend on the nature of the gas (as well as on the previous history of the metal) but not upon the actual gas pressure at the time of the experiment.

The variation of charge with pressure must thus be explained mainly in terms of the adsorbed gas layers. Each metal surface is certainly covered with a film but in the case of glass at ordinary temperature Langmuir⁽⁷⁾ has found that very little adsorption takes place. The glass surface in these experiments may then be taken as moving over a gas layer. Electrons will escape from the solid molecules more easily than from the gaseous, and the gas will become negatively charged, this charge being shared by the metal on which the layer exists. As the

gas pressure is reduced, the surface density of the adsorbed film will also diminish, though probably not in a linear manner. Langmuir (*loc. cit.*) finds in the case of glass and mica at low temperatures a variation of surface density with pressure of the form

$$m = \frac{ap}{1+bp},$$

where a and b are constants characteristic of the surface and of the gas. No reference to a corresponding variation in the case of metals was found, but such a formula might well be fitted to the observed results, assuming the charge produced by a given amount of rubbing to be proportional to the surface density of the adsorbed film.

At very low pressures the amount of gas adsorbed becomes negligibly small, and when this stage is reached the contact between the glass and the metal will become the more important factor. As the gas pressure is reduced to the lowest available limit, the glass-metal contact becomes more perfect, with a corresponding increase of charge.

For a given metal the relative charges in the different gases will depend partly on the respective ionization potentials of the gases, and partly on the relative surface densities of the adsorbed films. The ionization potentials for hydrogen, oxygen, and nitrogen do not differ sufficiently to show any distinction between the charges in these experiments, the available values being:—

Hydrogen	..	16.5 volts (H. D. Smyth),
Oxygen	..	15.5 volts (do.),
Nitrogen	..	16.9 volts (Foote and Mohler).

It is quite possible, however, that the difference between the charges is accounted for by differences in the amounts of the various gases adsorbed.

On this view the positive charge generated by ebonite on steel must be explained by assuming either (*a*) no adsorption on the ebonite, in which case it would be necessary for electrons to escape from molecules within the ebonite less readily than from the gaseous molecules adsorbed on the steel, or (*b*) greater adsorption on the ebonite than on the steel, in which case the conditions approximate to a metal surface rubbing over a gas layer adsorbed on ebonite. The first condition seems very

improbable, but no reference to the amount of adsorption on ebonite was available.

It would thus appear that except at extremely low pressures the true frictional effect is entirely masked by the presence of adsorbed films. Most other experimenters have employed much more vigorous methods of rubbing with the object of breaking through the films. The effect might be expected to be much less marked at higher temperatures, and a form of rubbing chamber suitable for such measurements is in process of construction.

Summary.

(1) In all the cases where a glass surface is rubbed on a metal the charge shows a marked variation with gas pressure, being a minimum over an approximate range from 1 to 10 mm.

(2) At the higher pressures the charge for given rubbing surfaces varies with the gas, but at very low pressures appears to be characteristic of the surfaces rather than of the gas.

(3) The relative variation of charge with gas pressure is independent of the capacity of the insulated system.

(4) The presence of mercury vapour in the friction chamber may lead to entirely false results.

(5) A suggested explanation of the results is based upon the presence of adsorbed gas films on the rubbing surfaces.

The experiments were carried out in the Physics Department of the University College of North Wales, Bangor, and the author is indebted to Professor E. A. Owen for placing at his disposal the necessary apparatus, as well as for much helpful criticism and advice.

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- (6) Kinsley, Phil. Mag. ix. pp. 692-706, May 1905.
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Bangor,
June 1929.

LXXXI. *The Effect of Variation in the Pressure of the Air and Dimensions of the Mouth on the Frequency of an Organ Flue-Pipe.* By A. E. BATE, M.Sc., Northern Polytechnic, London*.

ABSTRACT.

THE vortex theory of edge tones is shown to apply in the case of the mouth of an organ pipe in that $\frac{V}{n\bar{h}} = \text{a constant}$, where V is the velocity of the air jet, n is the frequency of the note, and h is the height of the mouth. If V is in feet per second and h is in feet, the constant is 2 for ordinary edge tones; whereas it is large in the case discussed, and is given by $\frac{74}{3}(0.3-s)$, where s is the thickness of the jet in inches. An explanation of the deviation is offered, and this indicates that the diameter of the vortices is the same for the three slit-widths used, at all frequencies, for the same value of h , but increases with increase in height of mouth.

§ 1. **A**N organ pipe is a coupled system, the components being the air jet and the air column. The action resembles that of Melde's experiment, the jet corresponding to the fork, and the air column to the string. It does not appear to be generally known that the resemblance is closer than it seems, for the pipe may be lengthened by a number of half wave-lengths while the same frequency prevails, provided the air pressure be the same throughout.

The writer's attention was first drawn to this fact by Dr. Clay, and led to the research described.

If a pipe of ordinary length be blown and pressure increased, the note is sharpened until it jumps to its first overtone. The reason is that the jet frequency is restrained by the column of air—and consequent change in end-correction—until the column breaks down into two half wave-lengths if open or three quarter wave-lengths if closed.

When a pipe several wave-lengths long is used, increase of air pressure does not cause the note to sharpen to the same extent, but to jump to a higher frequency, say from 256 to 340, depending on the length of the pipe; this is to be expected, since an extra node is more readily formed in a pipe containing 8 (say) nodes than in one containing 1 node, which is the number in the case first cited.

* Communicated by Dr. R. S. Clay.

Hence the jet decides the frequency when the pipe is long, and the pipe decides it when the latter is of normal length. It follows that the mouth conditions—chiefly the air pressure and height (sometimes called the cut-up)—may be varied considerably when a short pipe is used, the natural jet frequency being distorted by lengthening or shortening the pipe as required.

§ 2. The apparatus consists of the organ pipe, air supply and the means of measuring its pressure, and a standard for comparison.

The standards tried were (a) a hot-wire microphone; (b) a second organ pipe blown at constant pressure; (c) a tuning-fork, mounted on a box resonator.

The third was finally adopted. The advantage of (b) is that it maintains a constant wave-length whatever the temperature, any change in the frequency being the same in each pipe. It was, however, suspected of interfering with the adjustable pipe, and was therefore rejected.

The organ pipe used in these experiments consists of a brass pipe $2\frac{1}{2}$ in. internal diameter and .03 in. thick, 6 in. in length, extra lengths of pipe and sleeves of a larger diameter to join them to the first pipe, thereby enabling the length to be increased to any length up to 10 ft. The mouth of the pipe is cut in a plate $\frac{1}{2}$ in. thick fixed on to the end of the pipe and arranged so that the air jet passes across the pipe instead of along it. This allows the mouth to be adjusted without altering the length of the pipe above the lip, which would be the case in an ordinary organ pipe, for the adjustment is made by moving a sharp brass wedge forming the lip across the opening in the end plate. The air was obtained from an air compressor, which delivered it into a tank about 3 ft in diameter and 6 ft. high; then it passed in succession through two bottles of about $\frac{1}{4}$ ft. and 2 cu. ft. capacity respectively. From the latter it passed directly to the pipe through a short length of wide tubing. The inlet and outlet from this bottle are at opposite ends, and since the consumption of air never exceeds 3 cu. ft. per minute the velocity of the air along the bottle is of the order 2 ft. per minute. The drop in pressure or loss of head, therefore, is negligible, so that the pressure in the bottle, recorded by a water manometer communicating with the middle of the axis, is regarded as the velocity head, the static head being the atmospheric pressure. The pressures rarely exceed 4 in. of water, so that, taking atmospheric pressure as 400 in., the decrease of volume due to pressure

is less than 1 per cent., and is neglected in determining the velocity.

§ 3. Theoretically, the velocity of air at density ρ under an excess pressure P is found from the equation

$$P = \frac{1}{2}\rho V^2.$$

If the pressure be H , measured in inches of water, and the velocity V in ft. per sec., this becomes

$$V = 66.75 \sqrt{H}.$$

(Temperature and pressure effects are neglected, being small.)

Actually the velocity was determined by inserting a tested gas-meter in the air-pipe line between the two bottles and recording the rate of flow and pressure in the second bottle, first with a $\frac{1}{20}$ in. slit $1\frac{1}{2}$ in. wide and then with a $\frac{1}{40}$ in. slit of the same width. The results obtained are:—

	H.....	$\frac{1}{2}$ in.	$\frac{1}{2}$ in.	$\left[\frac{3}{4} \text{ in.} \right]$
(a)	V.....	24.75	35.07	40.40
	$\frac{V}{\sqrt{H}}$	49.5	49.61	46.66

The values of V were determined by dividing the volume passing per sec. by the area of the slit.

	H.....	$\frac{1}{2}$ in.	1 in.	2 in.	$\left[2\frac{1}{2} \text{ in.} \right]$
(b)	V.....	36.39	51.88	72.47	80.81
	$\frac{V}{\sqrt{H}}$	51.47	51.58	51.47	51.11

Above the value of H quoted the volume passing was outside the range of the gas-meter, and so the mean value of the first readings in each case are taken. They are 49.6 and 51.5 respectively. Calibration of the slits gave the $\frac{1}{40}$ in. slit correct to within 0.0003 in., $\frac{1}{20}$ in. slit = 0.0482 in. within 0.0003 in. Correcting the latter we get values of

$\frac{V}{\sqrt{H}} = 51.4$ and 51.5 respectively. The value of the constant, then, is 51.4 nearly, so that $V = 51.4 \sqrt{H}$.

This discrepancy is probably wholly accounted for by the contraction of the jet after leaving the slit, in which case the value of the vena contracta is 0.77.

§ 4. The process of matching jet and pipe frequencies is known as voicing the pipe, and is accomplished in practice

by expert "Voicers," who adjust the slit and alter the cut-up; but voicing was achieved by the writer as follows: the pipe, about 100 inches in length, was "stopped," *i.e.* the far end was closed by a flat plate. This had the effect of reducing the influence of the mouth upon the frequency of the air column. The air supply was adjusted to give a steady known pressure; then the height of the mouth was adjusted until the pipe gave a note near that required. The length of the pipe was then altered until the note agreed with that of the standard fork. It was usually necessary to readjust the lip to make the pipe speak as well as possible.

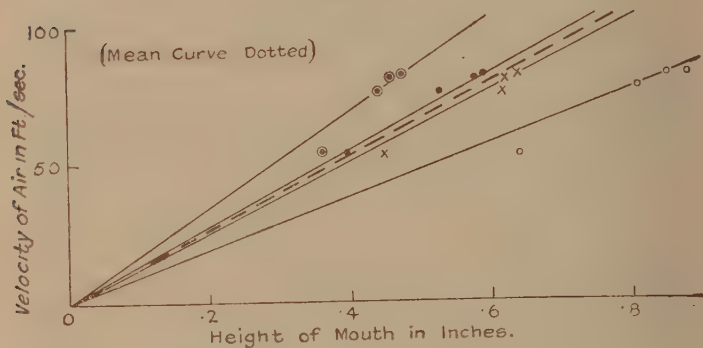
On moving the lip towards the slit, maintaining the same pressure, the frequency rises slightly (due, as we shall see later, to a change in the end-correction*), but remains nearly constant down to a certain height, at which the note jumps to a higher frequency; on moving the slit back again, the new frequency prevails to a considerable distance, but finally, at a certain height, resumes its former value. Continuing to open the mouth still more causes the tone to become flat, and again at a certain height a jump occurs, but to a lower frequency; on moving the lip once more to its original position, the initial frequency is suddenly regained. It was noticed that the two transition points at which the frequency returned to its former value were close together, and the position of the lip midway between them was taken as the position of maximum stability for that particular pressure and frequency. The transitions are obviously due to n (say) nodes in the pipe becoming $n+1$ and $n-1$ respectively. In some cases the jump was not back to its original frequency, but beyond it; in fact, in some instances it was impossible to return directly to the original note, so that mean point was selected from a curve connecting frequency and pressure. The curves for a frequency of 256 are shown in fig. 1, and it can be seen that the curve midway between the two inner curves is also midway between the two outer curves. This curve is the curve of maximum of stability. The velocity is proportional to the square root of the pressure, therefore the curves show that the increase above the mean velocity necessary to cause the note to jump to a higher frequency is equal to the decrease in velocity required to make it jump to a lower frequency. The return from these frequencies to the former also requires equal decrease and increase of velocities.

* See "Determination of the End Corrections at the Mouth of a stopped Organ Flue-Pipe," by author, to be published shortly.

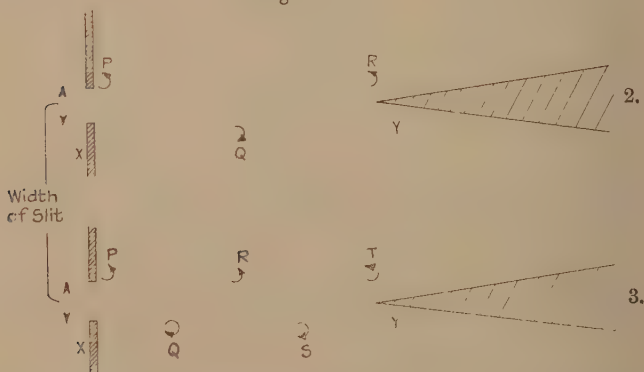
The portions of the graph between the two higher curves and between the two lower curves are areas in which the particular frequency (256) is unstable.

§ 5. The explanation of the sudden transition of the note is to be found in the phenomena of "edge-tones," investigated by Wachsmuth and König. These tones are formed

Fig. 1.



Figs. 2 & 3.



by a stream of air passing from a narrow slit and striking a sharp edge parallel to the slit.

The conditions governing the frequency of the tone are the distance from slit to edge, and the velocity of the air, suitable conditions producing a vortex system as shown in fig. 2. Assuming that air issues from the slit X, and strikes the edge Y, it has been shown that a vortex system is

formed such that when a vortex R passes Y, another, P, is formed on the same side of the air stream at the slit, and a third vortex has been formed the other side midway between P and Q. The frequency of the edge tone is equal to the number of vortices on one side of the jet which pass the edge per second. If U is the velocity of the vortex in the direction XY , and if $XY=h$, as $XY=PR$, $U=nh$.

The air on the outside of the vortex rows is at rest, so the jet must be moving with a velocity $2U$, so

$$V = 2U = 2nh$$

or

$$\frac{V}{nh} = 2,$$

where V is the velocity of the jet. This result has been verified by experiment. Increase of jet velocity beyond a certain point causes a rearrangement of the vortex system, as in fig. 3, in which twice the number of vortices pass Y per second. If V be the new velocity, and N the number of vortices passing on one side of the edge per second,

$$\frac{V'}{2Nh} = 2 = \frac{V'}{4nh} = \frac{V'}{2nh};$$

i. e. $V' = 2V$; so that double the velocity causes double the frequency, the mouth height h remaining unchanged. This also agrees with experiment. The same spacing of vortices may be obtained by moving the edge opposite to R (fig. 2) without altering the velocity of the air stream; XY will become $\frac{h}{2}$, and

$$\frac{V}{2nh} \text{ becomes } \frac{V}{2 \times 2n \times \frac{h}{2}},$$

and the frequency is $2n$, the octave, as before.

If the system be coupled with a column of air to form an organ pipe, the alternate vortices give rise to compressions which travel up the tube one quarter wave-length and return in time to augment the effect of the next vortex on the other side of the edge, or lip as it now becomes. On increasing the pressure to give rise to the system of fig. 3, the frequency is doubled and the pipe speaks the octave; if, however, the "cut-up" be halved, the octave is again elicited without the increase in pressure and therefore of velocity. *In the former case the octave is obtained by over-blowing; in the latter the pipe is normally blown.*

In the experiments described the jet is arranged to give its natural frequency.

§ 6. The pipe was voiced for different frequencies and pressures according to the method described above. The results, using the slit $\frac{1}{20}$ in. wide, $1\frac{1}{2}$ in. long, and a pipe

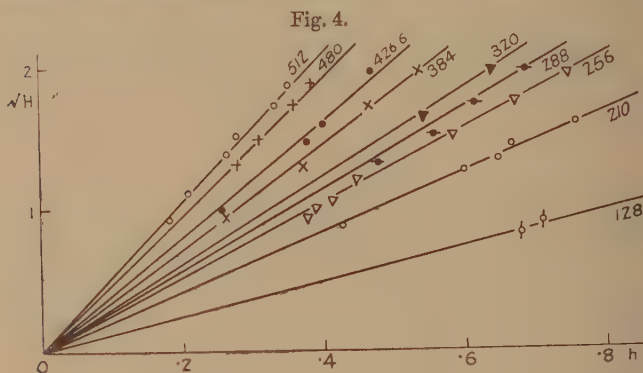
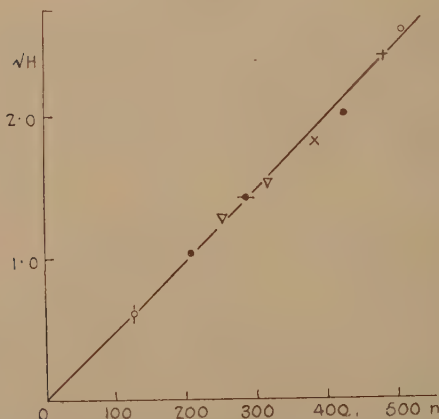


Fig. 5.



$2\frac{1}{8}$ in. diameter, are shown in figs. 4 and 5. The experiments were conducted at temperatures varying from about 57° F. to 62° F.; fig. 4 gives the curves connecting velocity and height of mouth for various frequencies, and fig. 5 shows the relationship between velocity and frequency for a fixed height of mouth of 0.5 in., the values having been taken

from fig. 4. In each case the curves are straight lines passing through the origin, so that $\frac{V}{h}$ and $\frac{V}{n}$ are constant; therefore $\frac{V}{hn} = \text{constant}$. If $P=1$ in., $n=200$, when $h=\frac{1}{2}$ in., and $\frac{V}{hn}=6.168$ for a slit $\frac{1}{20}$ in. wide.

Fig. 6.

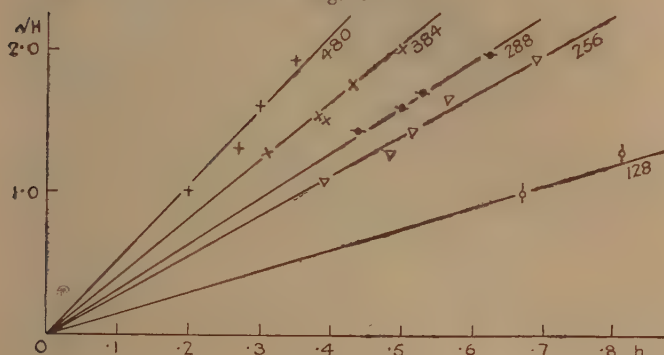
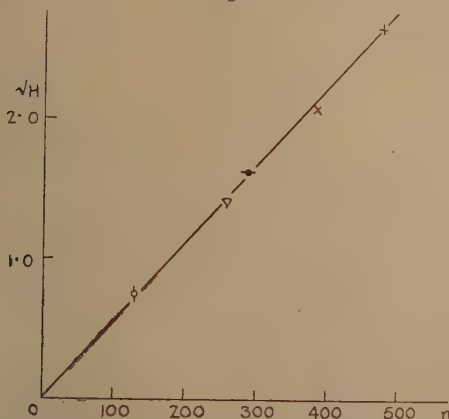


Fig. 7.



From § 5, $U=hn$, V being the velocity of the vortices; therefore $U = \frac{V}{6.168} = 0.16 V$, *i. e.* the velocity of the vortices is .16 that of the jet. This result is in close agreement with that obtained by Carrière*. He rendered

* Carrière, *Journ. de Phys. et Rad.* p. 61, Feb. 1925.

the vortices visible by a small jet of steam in the main jet and measured their velocity stroboscopically, and found it to be approximately 8 metres per second. He measured the jet velocity with a Pitot tube. It proved to be about 46 m. per second, so that for his experiment $V = 17 V$.

Fig. 8.

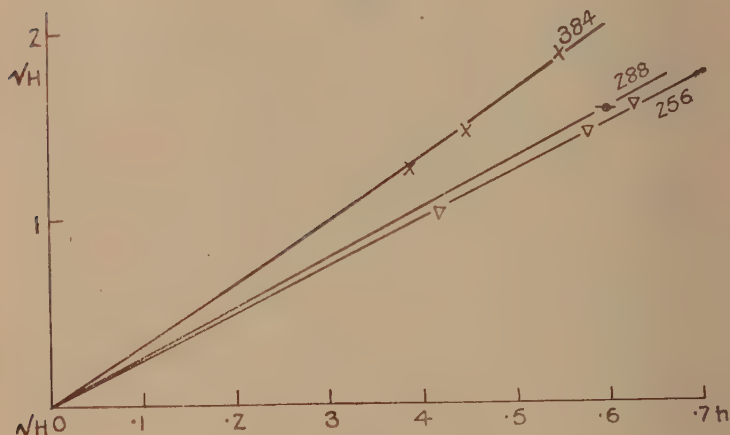
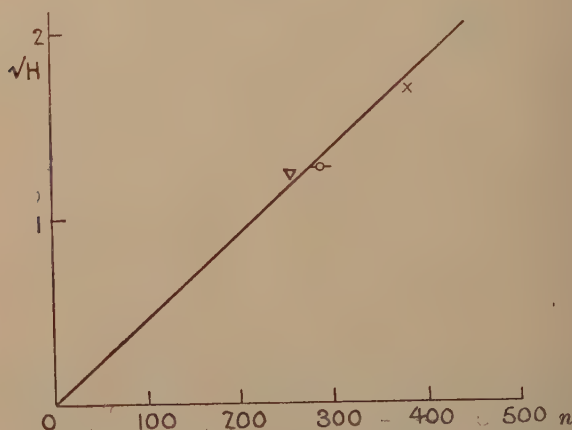


Fig. 9.



§ 7. Repetition with the $\frac{1}{40}$ in. wide slit, $1\frac{1}{2}$ in. long, and the same pipe, gave the results shown in figs. 6 and 7, which resemble figs. 4 and 5, but in this case $\frac{V}{nh} = 6.783$.

§ 8. Further results with a slit $\frac{3}{40}$ in. in width were sought, but the range was limited, only three sets of results being taken (figs. 8 and 9), and

$$\frac{V}{nh} = 5.55.$$

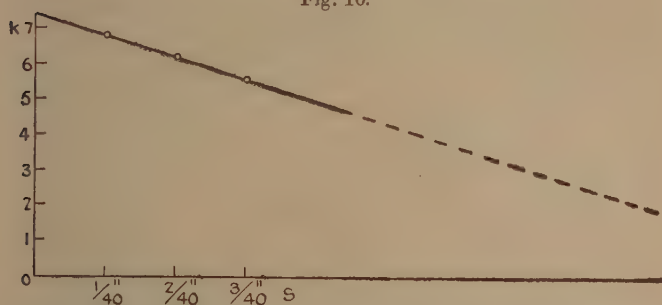
§ 9. The variation of $\frac{V}{nh}$ with slit-width is shown in fig. 10.

The result is a straight line of which the equation is

$$\frac{V}{nh} = \frac{74}{3} (0.3 - s),$$

where s denotes the width of the slit. The minimum value of $\frac{V}{nh}$ is 2, its theoretical value, when the value of s is 0.22.

Fig. 10.



§ 10. From § 3 the area of the vena contracta of the air jet appears to be about 0.77 that of the slit, and we may assume that this contraction is essentially in the thickness, since the ends of the slit are practically in line with the lower part of the pipe, which is connected to the air supply. The widths of the three jets are therefore taken as 0.02, 0.04, and 0.05 inch respectively.

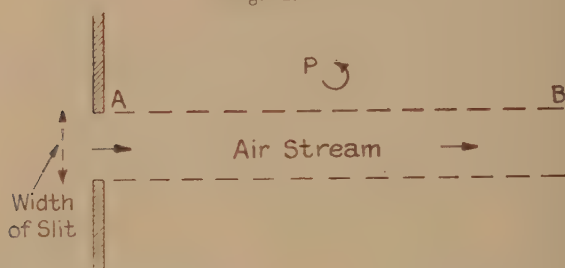
On issuing into the free air, the jet moves with a velocity depending on the pressure in the reservoir, and the free air next to the jet is dragged along, thereby tending to decrease the jet velocity and to form vortices. Vortices are formed, provided the jet velocity is above the critical velocity for turbulent flow.

Consider a vortex P (fig. 11) moving with a linear velocity U , at the side of a jet of velocity V , and parallel to it. The part of P farthest from AB is momentarily at rest, while that nearest AB is moving at a velocity $2U$,

the angular velocity and radius of a vortex being constant. From P to AB a viscous drag occurs; if d be the distance from the centre of P to AB (the edge of the jet), the rate of change of velocity $= \frac{V}{r+d}$; hence the centre of the vortex has a velocity of $\frac{V}{r+d} \cdot r$. This we have called U. It follows that

$$r = \frac{U}{V-U} \cdot d = \frac{d}{\frac{V}{U} - 1}.$$

Fig. 11.



For the narrowest slit,

$$\frac{V}{U} = 6.78,$$

and therefore

$$r = \frac{d}{5.78}.$$

It has been shown by Karman theoretically and verified by Benton experimentally that the distance between the centres of the avenues on each side of the jet bears a constant ratio to the distance between successive vortices in the same avenue. Karman gives 0.28 as the constant; Benton's value is 0.27. The distance between successive vortices is equal to the distance from slit to lip; hence for a mouth 0.5 in. high the distance between the centres of the avenues $= 0.14$ in., taking 0.28 as the constant. If the thickness of the jet from the narrowest slit be taken as 0.02 in., the distance

$$d = \frac{0.14 - 0.02}{2} = 0.06 \text{ in.},$$

so that

$$r = \frac{0.06}{5.78} = 0.01 \text{ in. nearly.}$$

For the slit $\frac{1}{20}$ in. wide,

$$d = \frac{0.14 - 0.04}{2} = 0.05 \text{ in.}$$

and

$$r = \frac{0.05}{5.16} = 0.01 \text{ in. nearly.}$$

For the $\frac{3}{40}$ in. slit,

$$d = \frac{0.14 - 0.06}{2} = 0.04 \text{ in.,}$$

so that

$$r = \frac{0.04}{4.55} = 0.01 \text{ in. nearly.}$$

If the mouth be 0.75 in. high, the distance between the avenues of vortices = 0.21 in., from which the values of d are respectively 0.095 in., 0.085 in., and 0.075 in., which give $r = 0.0164$ in., 0.0164 in., and 0.165 in. for the $\frac{1}{40}$, $\frac{1}{20}$, and $\frac{3}{40}$ in. wide slits respectively. It appears from these results that the vortices have a definite radius for a given height of mouth, and that this radius is independent of the thickness of the jet.

The author desires to acknowledge his indebtedness to Dr. Clay for the interest he has shown in this research.

References.

Sound,' by E. G. Richardson (published by Arnold). This contains an account of the work previously undertaken and copious references to original papers.

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LXXXII. *On the Electrification of a Two-dimensional "Ice-pail."* By W. B. MORTON, M.A., and MARY McDONALD, M.Sc., Queen's University, Belfast *.

THE two-dimensional analogue of Faraday's ice-pail is composed of an infinitely long parallel-sided strip for bottom, with two other strips of equal height to form perpendicular sides. When such an arrangement is freely charged, the electric field in the lower part of the interior becomes very small as the sides are raised. The question of the configuration of the field is here treated as an example of

* Communicated by the Authors.

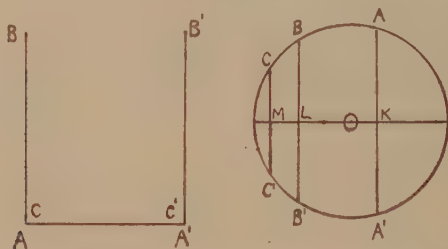
the general method of Schwarz, applicable to fields bounded by straight conductors. The work follows closely the procedure adopted in an earlier paper * on the electrification of two intersecting planes.

The field in the plane of z is represented on the interior of unit circle in a plane of ζ (fig. 1). To take advantage of the symmetry of the figure we make the points 0 and π on the circle correspond to the mid-points of AA' , CC' respectively. The differential relation between the complex variables is then

$$dz/d\zeta = C\zeta^{-2}(\zeta - e^{i\alpha})^{\frac{1}{2}}(\zeta - e^{-i\alpha})^{\frac{1}{2}}(\zeta - e^{i\beta})(\zeta - e^{-i\beta}) \\ (\zeta - e^{i\gamma})^{-\frac{1}{2}}(\zeta - e^{-i\gamma})^{-\frac{1}{2}}$$

where α, β, γ are the arguments of ABC .

Fig. 1.



To escape the appearance of a term in ζ^{-1} in the expansion for large values we require the relation

$$\frac{1}{2}e^{i\alpha} + \frac{1}{2}e^{-i\alpha} + e^{i\beta} + e^{-i\beta} - \frac{1}{2}e^{i\gamma} - \frac{1}{2}e^{-i\gamma} = 0.$$

$$\text{or} \quad \cos \alpha + 2 \cos \beta - \cos \gamma = 0.$$

This implies that β and γ are obtuse angles, and that the points are so placed that $OL = \frac{1}{2}MK$.

There are thus two independent constants, not counting the scale-constant C . One relation connecting these is obtained when we express the condition that the pail shall have a single bottom, *i.e.*, that $AB = CB$. The second relation is given by the shape of the pail, in the ratio of AB or CB to AA' .

For points on the conductors, which are represented by points on the circumference, we put $\zeta = e^{i\phi}$. The equation then reduces to $dz/d\phi = 2i(\cos \phi - \cos \beta)(\cos \phi - \cos \alpha)^{\frac{1}{2}}(\cos \phi - \cos \gamma)^{-\frac{1}{2}}$.

* Phil Mag. i. p. 337 (1926).

The single-bottom condition is expressed by the vanishing of the integral for z between limits of γ and α for ϕ . As a preliminary to mechanical quadrature, the integral is transformed by the substitution

$$\cos \phi = \cos \gamma \cdot \cos^2 \theta + \cos \alpha \cdot \sin^2 \theta.$$

This does away with the infinite value of the integrand at the lower limit, and makes the range from 0 to $\frac{1}{2}\pi$. To get pairs of corresponding values of the constants, a definite value was given to $\cos \alpha$, and the integrand was then plotted for a number of values of $\cos \gamma$ lying between $-\cos \alpha$ and -1 . The positive and negative parts of the areas having been found by planimeter, it was possible to find by interpolation the value of $\cos \gamma$ which made the total area vanish. The shape of the pail could then be found by evaluating the integrals representing the base and the height.

The following values were obtained:—

$\cos \alpha =$	$\cdot 2$	$\cdot 4$	$\cdot 6$
$-\cos \gamma =$	$\cdot 551$	$\cdot 893$	$\cdot 9943$
side/bottom =	$\cdot 052$	$\cdot 225$	$\cdot 633$

From the figures in the last column it will be seen that there is a practical difficulty in the way of getting a form which looks like an ice-pail. If the sides are to be made taller in comparison with the breadth, we shall have to work with values of $\cos \gamma$ lying very close to -1 .

The angles of $\alpha \beta \gamma$ give directly the distribution of the total charge between the different parts of the surface, the charge between two points being represented by the arc of the circle between the corresponding points on the ζ -diagram. So each side-plane carries the fraction $(\beta - \alpha)/2\pi$ on its outer, and $(\gamma - \beta)/2\pi$ on its inner surface, while the bottom has α/π on its under surface and $(\pi - \gamma)/\pi$ on its upper surface. The distributions for the three shapes given above are shown on fig. 2, where the fractional charges are represented as segments of the unit vertical height of the figure, plotted against the shape-ratio, of height to diameter of base. The trend of the curves drawn through the points indicates the ultimate transfer of the whole charge to the outsides of the two side-planes as the height of these is increased. It may be noted that the charge borne on the inner surfaces of the side-planes passes through a maximum value.

Fig. 3 shows the forms of the equipotentials and lines of force for the last of the three forms examined. These are the graphs of $\log \rho = \text{const.}$ and $\phi = \text{const.}$, where $\zeta = \rho e^{i\phi}$.

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The equipotentials are $\rho = .9, (.9)^2, (.9)^3, (.9)^4$, and the lines of force correspond to 5° intervals in ϕ . To obtain the former, mechanical quadrature was applied to the expressions

Fig. 2.

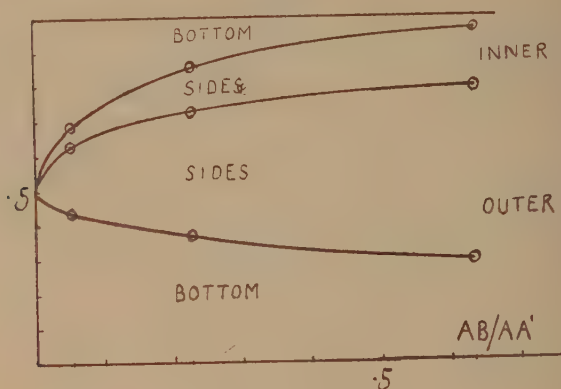
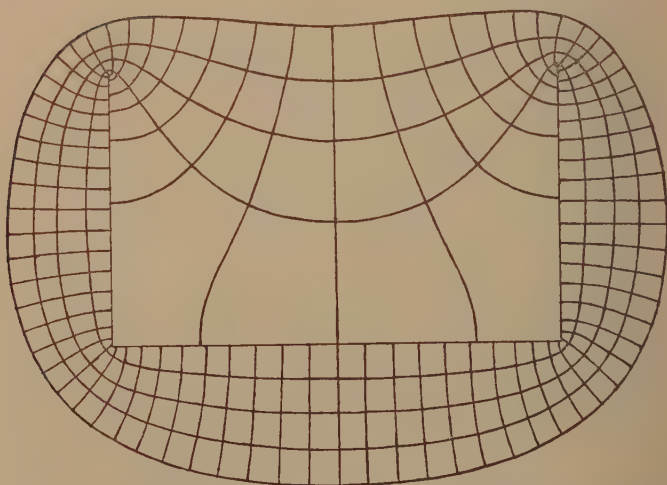


Fig. 3.



for $\partial x/\partial \phi, \partial y/\partial \phi$ given by the fundamental equation. The lines of force were got by joining points with the same ϕ on the different equipotentials.

LXXXIII. *A Method for the Magnetic Analysis of a Spectrum by means of Unresolved Zeeman Patterns, and its Application to Ag II.* By A. G. SHENSTONE, M.A., Ph.D., and H. A. BLAIR, M.Sc.*

ABSTRACT.

A METHOD of determining the Landé g -values from unresolved Zeeman patterns is discussed. The method is applied to the spectrum of Ag II., and the cases where the measured values disagree with the theoretical are considered with regard to the usefulness of g -values as compared with intensities as criteria in the identification of terms.

THE magnetic factors " g " for the terms of a spectrum are known in few cases with any completeness. In general we do not have a complete magnetic analysis because of the fact that it is not possible to obtain patterns of weak lines with the very high resolving power necessary for such work. It should be useful, however, to obtain such complete analyses, even though accuracy is sacrificed for completeness. Such an analysis of the silver spark spectrum is here presented.

The experimental arrangements were very simple. A silver arc was run in air between the poles of a magnet giving about 34,000 gauss. The light was passed through a quartz double-image prism and then through a quartz lens which focussed the two images, one above the other, on the slit of a Hilger E1 quartz spectrograph. This instrument has shown a resolving power at $\lambda 2500$ of approximately 40,000. The exposures varied from a few seconds to about one half-hour.

The Zeeman patterns obtained were all unresolved except two; and it is necessary, therefore, to consider the means of obtaining g -values from such patterns. To do this we can use the theoretical intensity formulæ given by Hönl † in order to calculate the centre of intensity of an unresolved pattern.

The formulæ for the intensities of the Zeeman components for the case of $\Delta J = -1$ are as follows:—

$$\begin{aligned} A_{M\pm 1}^M &= C \frac{1}{2} (J \mp M)(J \mp M - 1) & \sigma\text{-components,} \\ A_M^M &= C (J^2 - M^2) & \pi\text{-components,} \end{aligned}$$

* Communicated by the Authors.

† *Z. Physik*, xxxi. p. 340 (1925).

where C represents a factor independent of M . The centre of gravity of the π -components is obviously at the undisplaced position of the line since I_M^M has its maximum for $M=0$. The intensities of successive σ -components are in the ratios

$$(J+J)(J+J-1):(J+J-1)(J+J-2)::\dots:\{J-(J-2)\}\{J-(J-2)-1\}$$

i. e. $2J(2J-1):(2J-1)(2J-2)::\dots:3.2:2.1.$

If we take the distance between the strongest and weakest components as unity, then, using the principle of moments, the centre of intensity, measured from the weakest component, is given by

$$X = \frac{1}{2J-2} \left\{ \frac{1.2.3 + 2.3.4 + \dots (2J-2)(2J-1)2J}{1.2 + 2.3 + \dots + (2J-1)2J} \right\}.$$

The two finite series may be summed with the result,

$$X = \frac{1}{2J-2} \left\{ \frac{\frac{1}{4}(2J-2)(2J-1)2J(2J+1)}{\frac{1}{3}(2J-1)2J(2J+1)} \right\} = \frac{3}{4},$$

independently of J . The distance of the weakest component from the position of the original line is $(J-1)g_2 - (J-2)g_1$, and the distance between the weakest and strongest components is $(g_1 - g_2)(2J-2)$. Therefore, the centre of intensity should be at a distance from the undisplaced position equal to

$$\begin{aligned} & (J-1)g_2 - (J-2)g_1 + \frac{3}{4}(g_1 - g_2)2(J-1) \\ & = \frac{1}{2}\{g_1(J+1) - g_2(J-1)\}. \end{aligned}$$

This simple result may be used in cases of either odd or even multiplicities and $g_1 \lesseqgtr g_2$. It should be noted that J in the formula is the greater of the two J 's involved, and that g_1 belongs to the same level as J . The use of this formula depends upon the assumption that the centre of intensity is the point on which the observer sets the cross-hairs of his measuring instrument. In practice it has been found that this assumption is justified if the pattern is sufficiently far from complete resolution, *i. e.*, the method gives the most nearly correct results where $g_1 - g_2$ is not too great.

The formulæ for intensities of Zeeman components in the case of $\Delta J=0$ are :

$$\begin{aligned} A_{M\pm 1}^M &= C' \frac{1}{2}(J \mp M)(J \pm M + 1) & \sigma\text{-components,} \\ A_M^M &= C'M^2 & \pi\text{-components.} \end{aligned}$$

The σ -components have intensities in the ratios,

$$2J.1 : (2J-1)2 : (2J-2)3 : : : 1.2J,$$

i. e., the pattern is symmetrical about its own centre. This centre lies at a distance from the undisplaced line equal to $\frac{1}{2}(g_1 + g_2)$ for either odd or even multiplicity. Twice the measured displacement of such a line, therefore, gives directly the sum of the two g 's.

The π -components have intensities in the ratios,

$$(a) \quad 1^2 : 2^2 : : : J^2 \quad \text{for odd multiplicity,}$$

and

$$(b) \quad 1^2 : 3^2 : : : (2J)^2 \quad \text{for even multiplicity.}$$

In the two cases, taking the distance from the weakest component to the strongest component as unity, the centre of gravity measured from the weakest component is :

$$(a) \quad y = \frac{1}{J-1} \cdot \frac{1 \cdot 2^2 + 2 \cdot 3^2 + \dots + (J-1)J^2}{1^2 + 2^2 + \dots + J^2}$$

$$= \frac{1}{J-1} \cdot \frac{\frac{J}{12}(3J+2)(J+1)(J-1)}{\frac{J}{6}(J+1)(2J+1)}$$

$$= \frac{1}{2} \frac{3J+2}{2J+1}$$

$$(b) \quad y' = \frac{1}{J-\frac{1}{2}} \cdot \frac{1 \cdot \frac{3^2}{2} + 2 \cdot \frac{5^2}{2} + \dots + (J-\frac{1}{2})J^2}{\frac{1^2}{2} + \frac{3^2}{2} + \dots + J^2}$$

$$= \frac{1}{J-\frac{1}{2}} \cdot \frac{\frac{1}{192}(2J-1)(2J+1)(12J^2+16J+3)}{\frac{1}{6}(J+1)(2J+1)J}$$

$$= \frac{1}{16} \frac{12J^2+16J+3}{J(J+1)}.$$

The expressions for the centre of intensity measured from the undeviated position are as follows :—

(c) $(g_1 - g_2) + y(J-1)(g_1 - g_2) = (g_1 - g_2)\{1 + y(J-1)\}$
for odd multiplicities.

(d) $\frac{1}{2}(g_1 - g_2) + y'(J-\frac{1}{2})(g_1 - g_2) = (g_1 - g_2)\{\frac{1}{2} + y'(J-\frac{1}{2})\}$
for even multiplicities.

As the expressions for the centre of gravity are complicated, it is more useful to tabulate the values of y and y' , and use the formulæ c and d .

TABLE I.

Even Multiplicities.		Odd Multiplicities.	
J	y'	J	y
$\frac{1}{2}$...	1	...
$1\frac{1}{2}$	·90	2	·80
$2\frac{1}{2}$	·84	3	·79
$3\frac{1}{2}$	·82	4	·78
$4\frac{1}{2}$	·80	5	·77
$5\frac{1}{2}$	·79	6	·77
∞	·75	7	·76
		∞	·75

In practice the measurements of the π -components are used only as a check on the more accurate results obtained from the σ -components.

The spark spectrum of silver has been analysed by Majumdar*, McLennan and McLay†, and Shenstone‡. The second and third analyses are in agreement, but the last is the more complete and is, therefore, used here.

If g -values are to be obtained from unresolved patterns it is obviously necessary to know one of the two g 's for each line. In the case of Ag II. the start can be made from the two resolved patterns found, viz.:

$$5s^3D_1 - 5p^3P^{\circ}_1 \quad (\cdot 95) - 1\cdot 50 \quad \text{Landé } (1\cdot 00) \cdot 50, 1\cdot 50$$

$$5s^3D_1 - 5p^3P^{\circ}_2 \quad (\bar{0} \ 1\cdot 00) - 2\cdot 49 \quad \text{,,} \quad (\bar{0} \ 1\cdot 00) \ 1\cdot 50, \bar{2}\cdot 50.$$

The measurements are the average of a large number made on several plates. Dashes indicate components which were present but whose measurements would not add to the accuracy. A number of Cu I. and Cu II. lines were used as standards and were found to be consistent.

It was assumed that the patterns given above differed from the predicted pattern only because of errors of measurement and that, therefore, the g -values for the three terms involved are the Landé values. Knowing these three g 's it is then possible, by means of the formulæ developed above, to calculate from the measured unresolved

* Majumdar, Indian Journal of Physics, ii. p. 15 (1928).

† McLennan and McLay, Trans. Roy. Soc. Can. xxii. p. 10 (1928).

‡ Shenstone, Phys. Rev. xxxi. p. 317 (1928).

patterns, the g -values of all the remaining terms. Because of the rather large errors of measurement of the narrow patterns, a method of successive approximation for the g -values was adopted. This involved, first, a calculation of g 's from single lines, and afterwards an adjustment of the values to give the best fit to all the lines involving each term. Naturally the values obtained by such a process will have probable errors which will be smaller, the larger the number of lines from which they are calculated. Judging from the range of values obtained for any particular g , the error in those determined from more than five lines should not be higher than three per cent. The variation of the calculated values of g for a single term is illustrated by the following set whose average was used for the g of $5s^1D_2$:

1.00, 1.03, 1.04, 1.04, 1.01, 1.05, 1.07.

Table II. (p. 770) gives the g -values calculated, the Landé g 's, the number of lines used in each case, and the g -sums for terms of the same J and configuration.

The following points are important :—

(1) The g -sum rule is fulfilled within the experimental error. The almost exact agreement for the terms of structure $4d^95d$ is, of course, fortuitous.

(2) The g -values of most of the terms are reasonably near the Landé values with the following exceptions :—

(a) Terms of the structure $4d^95p$ and $J=2$.

(b) Terms of the structure $4d^95d$ and $J=2$ and $J=1$.

The fact that the g -values for the terms just mentioned depart so markedly from the Landé values involves an important theoretical question, viz.: the relative weight which is to be assigned to the g -values and to the intensities of combinations in the designation of the levels of a spectrum. For instance, in the case of the terms of $J=2$ in the structure $4d^95p$, the four levels could be named in such a way as to make the individual g 's most nearly the Landé values. This would involve a complete sacrifice of the ordinary intensity rules as well as a much greater departure from the interval rule. It would also involve great difficulties in the interpretation of iso-electronic sequences. For example, the term which is now $5p^3D^{\circ}_2$ in Ag II. would have to be chosen as $5p^3F^{\circ}_2$, whereas in Pd I. the equivalent term would be chosen as $5p^1D^{\circ}_2$.

The same theoretical difficulty presents itself in the case of series of terms of two multiplicities converging to the same multiple limit. A case in point is that of the terms

$5s^3$ and 1D and $6s^3$ and 1D in the spectrum under discussion. Theoretically, as we proceed to higher series members, the

TABLE II.
Ag II. g -values and g -sums.

Term.	g .		No. of Lines.	Structure.	J.	g -sum.	
	Landé.	Obs.				Landé.	Obs.
$5s^3D_3$	1.33	1.33	4	$4d^35s$	1	.50	.50
$5s^3D_2$	1.17	1.13	7		2	2.17	2.16
$5s^3D_1$.50	.50	7		3	1.33	1.33
$5s^1D_2$	1.00	1.03	7				
$5p^3P^o_2$	1.50	1.50	5	$4d^35p$	1	3.00	3.00
$5p^3F^o_3$	1.08	1.08	7		2	4.34	4.49
$5p^3P^o_1$	1.50	1.50	7		3	3.41	3.43
$5p^3F^o_1$	1.25	1.26	4		4	1.25	1.26
$5p^3D^o_4$	1.17	.87	7	$4d^36s$	1	.50	.53
$5p^3P^o_3$	—	—	3		2	2.17	2.22
$5p^3D^o_3$	1.33	1.25	8		3	1.33	1.34
$5p^3F^o_2$.67	.92	7				
$5p^1F^o_3$	1.00	1.10	7	$4d^35d$	1	5.00	4.99
$5p^1P^o_1$	1.00	1.00	8		2	4.34	4.35
$5p^3D^o_1$.50	.52	4		3	4.16	4.23
$5p^1D^o_2$	1.00	1.20	5		4	3.30	3.35
					5	1.20	?
$6s^3D_3$	1.33	1.34	3				
$6s^3D_2$	1.17	1.11	4				
$6s^3D_1$.50	.53	3				
$6s^1D_2$	1.00	1.11	4				
$5d^3S_1$	2.00	1.84	2				
$5d^3G_5$	1.20	?					
$5d^3G_4$	1.05	1.03	2				
$5d^3P$	1.50	1.37	1				
$5d^3P_1$	1.50	.90	2				
$5d^3D_3$	1.33	1.34	2				
$5d^3F_3$	1.08	1.04	3				
$5d^3D_2$	1.17	1.07	3				
$5d^3S_0$	—	—	1				
$5d^3F_4$	1.25	1.26	3				
$5d^1P_1$	1.00	1.51	3				
$5d^3G_3$.75	.75 ?	2				
$5d^3D_1$.50	.74	2				
$5d^1G_4$	1.00	1.06	1				
$5d^1D_2$	1.00	1.20	2				
$5d^3F_2$.67	.71	2				
$5d^1F_3$	1.00	1.10	2				
$5d^3P_0$	—	—	0				

Total No. of Lines = 72.

electron couplings change in such a way as to dissolve the identity of the singlet term as it approaches the triplet. The g -sum of 3D_2 and 1D_2 should, therefore, be shared in

some undetermined way and the differentiation of the two levels should decrease, bringing in a relative increase of the intensities of inter-system combinations. In point of fact the g -values do become equal, but the identities of the two levels do not fuse, but become more distinct when intensities are used as the criterion. In other words the naming of these terms by Zeeman effects is impossible, but it can be done uniquely from the intensities of their combinations. To illustrate this point we can compare the relative intensities of the inter-system combinations of the 1D_2 with its singlet combinations. Table III. contains these quotients for a number of spectra of the same type as Ag II., and also for the d^ns^2F series terms of Pd II. and Ni II.

TABLE III.
Ratios of Inter-system to Intra-system Intensities.

Spectrum.	Series Member.			1st member.
	1	2	3	Last member.
Cu II.	2.18	.37		5.4
Ag II.	1.45	.27		5.8
Au II.	1.33	.38		3.5
Ni I.	.54	1.66	0 *	∞
Pd I.	1.33	1.73	.33	4.0
Ni II.	.58	.015		Very large.
Pd II.	1.12	.007		Very large.

It is obvious that in every case the intensities of the inter-system combinations fall off much more rapidly for the higher series members than do the intra-system combinations. The apparent increase of the inter-system intensities in the second member for Ni I. and Pd I. is explained by the fact that the second member singlet combinations are in the extreme red, where intensities are quite unreliable.

The method used for the summing of the finite series in this paper is due to Sir Isaac Newton, through Dr. E. U. Condon, who must be Sir Isaac's proxy in the reception of our thanks.

Palmer Physical Laboratory,
Princeton University, N.J.,
6th March, 1929.

* H. N. Russell, Phys. Rev. xxxiv. p. 821 (1929).

LXXXIV. *On the Origin of the Spark Lines in X-ray Spectra.*
By B. B. RAY, D.Sc., Calcutta University.

1. *Introduction.*

BESIDES the characteristic X-ray emission lines of an atom, there are a large number of lines in the X-ray spectra of the elements which do not follow the well-known Moseley law, and are named as "non-diagrammatic" lines. After Kossel's satisfactory explanation of the process for the production of the characteristic emission lines of the atoms, Wentzel suggested that the non-diagrammatic lines might originate from an ionized atom, namely, these lines arise from an excitation process in which more than one electron is removed from the inner levels of the atom. From the close resemblance to conditions necessary for the production of the spark lines in the ordinary optical spectra, Wentzel † suggested the name of spark lines to these lines. The characteristic features of these spark lines are:

(a) They accompany a prominent emission line, and generally lie on the shorter wave-length side of the latter. Thus we may have spark lines connected with the lines $K\alpha$, $K\beta$, $L\alpha$, $L\beta$, $M\alpha$, and so on.

(b) They are broad and diffuse, and Coster (Phil. Mag. xlv. p. 546, 1922) is of opinion that these spark lines may consist of unresolved components.

(c) Systematic measurements of the intensity of these lines could not be made with the change in voltage in the X-ray tube, as they are very weak.

Experiments for the proper understanding of the problem of production of these satellites have been made by Bäcklin ‡ for $K\alpha$ -satellites of Al, and Siegbahn and Larson § for $L\alpha$ -satellites of Mo, where they have carefully studied the production of these lines, maintaining a constant voltage in the tube, and have shown:

1. That the spark lines are produced at an exciting voltage slightly above, and certainly at much less than twice the critical voltage of, the K- or the L-level, as the case may be

* Communicated by the Author.

† Siegbahn, 'The Spectroscopy of X-rays.'

‡ Zeit. f. Phys. xxvii. (1924).

§ Ark. f. Mat. Astrooch. Fys. xviii. No. 18 (1924).

2. That all the spark lines appear simultaneously, and that with different voltage the intensity relations of the lines do not change.

3. That at a critical voltage greater than twice the critical voltage necessary to excite the K- or L-lines no new lines appear.

To account for the production of the $K\alpha$ -satellites, Wentzel assumes that the atom may either lose two electrons from the K-shell, or one from K and others from L- or M-shells, and so on. The transition processes giving rise to the various lines may be illustrated as follows, by making use of the structure diagram :—

K-satellites :

$$\begin{aligned}\alpha_3 \dots & 2K6L_2 \leftarrow 1K7L_2, \\ \alpha_4 \dots & 1K5L_2 \leftarrow OK6L_2, \\ \alpha_5 \dots & 2K5L_2 \leftarrow 1K6L_2, \\ \alpha_6 \dots & 1K5L_2 \leftarrow OK7L_2, \\ \alpha' \dots & 2K7L_2m-1 \leftarrow 1K8L_2m-1.\end{aligned}$$

In favour of Wentzel's supposition may be cited the fact that his prediction that $\Delta\nu$ values for $\alpha_5 - \alpha_3$ should equal that for $\alpha_3 - \alpha_1$, and $\alpha_6 - \alpha_4$ should be equal to $\alpha_3 - \alpha_1$ for the next higher element. These conditions are fulfilled in the measurements of Wetterblad* on the spark lines of Mg, Al, and Si. Following Wentzel, Druyvesteyn† obtained the relation

$$(K\beta'' - K\beta_1)z = (L - M)_{z+1} - (L - M)_z,$$

where $K\beta''$ is the satellite of the $K\beta_1$ -line, and showed that the relation conforms to experimental results. But the extension of the relation to L-satellites gave less satisfactory results.

Richtmeyer‡ has recently discussed the whole question of X-ray spark lines, and has shown that neither Wentzel's theory nor Druyvesteyn's suggestion does really explain all the facts known about these lines. He has suggested "the hypothesis that these satellites are produced by two-electron transfers, similar to the primed lines (terms) in optical spectra," and "that the line $K\alpha_4$ is the result of the simultaneous jump of one electron from the L_{II} level to a vacancy in the K shell, and of another electron from an optical level to a vacancy in the M shell, both transfers cooperating to emit a single quantum," but no suitable choice of combination

* *Zeit. f. Phys.* xlii. (1927).

† *Phil. Mag.*, July 1928.

‡ *Dissertation*, Groningen (1928).

of frequencies could be made in any atom to get the right result, even qualitatively.

2. Suggested Interpretation.

Saha and Ray * have pointed out that, in order to explain the origin of the characteristic emission lines of an atom, the subdivision of L_2 , M_2 , N_2 into two statically distinct levels such as $L_{21}L_{22}$, $M_{21}M_{22}$, $M_{32}M_{33}$, $N_{21}N_{22}$,, and so on, is unwarranted, and such subdivision is opposed to the structure of the outer shells as revealed by the analysis of optical spectra. The division of such sublevels as $L_{21}L_{22}$, $M_{32}M_{33}$, etc., appears by the synthesis of the quantum characteristic of the electrons according to the Pauli-Hund principle, as is usually done in the analysis of the optical spectra.

Thus, in order to explain the $K\alpha_1$ and $K\alpha_2$ radiations, we consider transition of the type $K_16L_2 \rightarrow 2K_15L_2$, which gives us $K\alpha_1$ and $K\alpha_2$ (K gives 2S , $6L_2$ gives 1S_0 , and the resultant is 2S_1 ; similarly $2K_1$ gives 1S_0 and $5L_2$ gives 2P_1 , 2P_2 and the resultant is 2P_1 , 2P_2).

During the process of transition from $L_2 \rightarrow K$ we have two lines, $K\alpha_1$, and $K\alpha_2$, corresponding to $^2S_1 \leftarrow 2P_1$, $^2S \leftarrow 2P_2$.

The origin of lines $K\beta_1$, $K\beta_2$ in the K series, and all the lines in L or M series, could be similarly explained.

According to this method, Wentzel's suggestion for the origin of the $K\alpha$ satellites is defective, inasmuch as he neglects the multiplicity of terms arising in such process. Thus, for $K\alpha_3$ Wentzel suggests transition of the type $1K7L \rightarrow 2K6L$. In this process the Pauli-Hund principle demands a larger number of lines than what Wentzel considers. The number of terms arising out of such transition will depend on the actual transference of the electron from L_1 or L_2 level. Moreover, the argument that all the lines arising out of such process will be crowded at $K\alpha_3$ cannot be true, as the separation of the terms in this transition will be more marked than the characteristic emission lines ($K\alpha_1$ and $K\alpha_2$), because of the increase of the net central charge in the ionized atom. Further, according to Wentzel, the intensity relation between the spark lines should change with the change in the existing voltage, but Bäcklin's and Siegbahn and Larson's observations for the $K\alpha$ and $L\alpha$ satellites of Al and Mo respectively are directly opposed to this contention. On the experimental evidences put forward by Siegbahn and Larson † and Bäcklin ‡ that all the spark

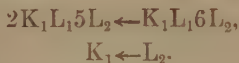
* *Phys. Zeits.* xxviii. (1927).

† *Loc. cit.*

‡ *Loc. cit.*

lines are produced simultaneously, we suggest the following scheme*.

Let us suppose that in the process of excitation two electrons are ejected simultaneously—one from K_1 , the other from L_1 —and that there is now a rearrangement in which one electron passes from L_2 to K_1 . The transition is



According to the Pauli-Russel-Hund theory,

the left-hand side gives ${}^3P_{012}$, 1P_1 ,

the right-hand gives 3S_1 1S_1 .

We now expect a multiplet consisting of 6 lines, as follows:—

$\frac{2K_1L_15L_2}{K_1L_16L_2}$	1P_1	3P_0	3P_1	3P_2
3S_1	α_3	α_4	α_6	\times
1S_0	α^1		α_5	

In the table of P terms (p. 776) we are arranging the known spark lines on this basis. There are other alternative arrangements possible, but for theoretical reasons we prefer the present one.

In the scheme the line ${}^3S_1-{}^2P_2$, which ought to be the strongest, is missing. But this simply means that the difference of ${}^3P_1-{}^3P_2$ is very small, and cannot be separated on the plate. Thus α_6 is a composite line which is confirmed by its appearance on the plate as a strong and diffuse line.

There is nothing improbable in such an assumption. We get a similar example in the arc spectrum of He. The combination K_1L_2 gives us ${}^1P_1{}^3P$, but the 3P set generally appears as a doublet term. It is only recently that Houston† and Burger‡ have been able to show that the 3P difference is extremely small. In fact Houston found $\Delta\nu$ for ${}^3P_0-{}^3P_1=-\cdot992$, and ${}^3P_1-{}^3P_2=-\cdot071$. The terms in He are inverted, *i. e.*, ${}^3P_0 < {}^3P_1 < {}^3P_2$.

* A further objection against Wentzel's suggestion is that he puts more electrons in the L_2 -level than can be allowed by Pauli's principle. For example, Wentzel puts seven electrons in L_2 , whereas, according to Pauli, it cannot contain more than six.

† Phys. Rev. xxix. p. 749.

‡ *Zs. f. Phys.* xxxviii. p. 437.

3. The ${}^3S_1-{}^1S_0$ Differences.

The ${}^3S_1-{}^1S_0$ terms arise from the coupling K_1L_1 , which we obtain in the spectrum of helium. It has been empirically found that the difference ${}^3S-{}^1S_0$ varies directly as the charge on the nucleus.

TABLE of P terms in ν/R (unit).

		3P_0 .	3P_1 .	3P_2 .	1P_1 .	Ordinary doublet, ${}^2S_{\frac{1}{2}}-{}^2P_{\frac{1}{2}}$.	K- absorption limits in ν/R .
Na	$\left\{ \begin{array}{l} {}^3S_1 \\ {}^1S_0 \end{array} \right.$	77.32		77.98	77.22	K α	
			$\swarrow \searrow$ 77.77		$\uparrow \downarrow$ 76.99		
Mg	$\left\{ \begin{array}{l} {}^3S_1 \\ {}^1S_0 \end{array} \right.$	93.14		93.90	92.28	92.34	95.81
			$\swarrow \searrow$ 93.66		$\uparrow \downarrow$ 92.75	$\frac{\Delta\nu}{R} = .02^*$	
Al	$\left\{ \begin{array}{l} {}^3S_1 \\ {}^1S_0 \end{array} \right.$	110.46		111.29	110.25	109.53	114.67
			$\swarrow \searrow$ 110.01		$\uparrow \downarrow$ 109.99	$\frac{\Delta\nu}{R} = .03^*$	
Si	$\left\{ \begin{array}{l} {}^3S_1 \\ {}^1S_0 \end{array} \right.$	128.19		130.13	129.0	128.18	
			$\swarrow \searrow$ 129.93		$\uparrow \downarrow$ 128.66	$\frac{\Delta\nu}{R} = .04^*$	
P	$\left\{ \right.$					148.4	158.26
						$\frac{\Delta\nu}{R} = .06^*$	
S	$\left\{ \right.$					170.0	181.81
						$\frac{\Delta\nu}{R} = .09^*$	
Cl	$\left\{ \right.$					193.1	207.84
A	$\left\{ \right.$						235.73
K	$\left\{ \right.$						265.33

Taking the K_1L_1 coupling in the present case as being perfectly analogous to that of He, the central charge being 11, 12, 13 ... for Na, Mg, and Al ... and assuming that the outer electrons are without effect on the coupling, we find that the $\Delta\nu$ separations ${}^3S_1-{}^1S_0$ do actually vary as Z .

* Calculated from Sommerfeld's formula.

	$^3S_1 - ^1S_0.$	$\frac{\Delta\nu}{RZ}.$
He	$\frac{6422}{109765}$	·029
Na	·22	·020
Mg	·24	·020
Al.....	·26	·020

4. Reasons for assigning the larger difference to the L_15L_2 Coupling.

We have assigned the larger difference to $^1P-^3P$ differences arising from L_15L_2 coupling for the following reasons. In the former case, $1Z, K_1L_1$, the electrons were in orbits having different values of the total quantum number n . Hence the effect of coupling is slight. In the present case $n=2$ for both sets, and the effect of coupling will be to produce very large separations in the $^1P-^3P$ values. As a matter of fact, this hypothesis is borne out by facts in optical spectra.

The actual values of the separation caused by the coupling L_1xL_2 ($x=1, \dots 6$) in the optical spectra of the group Be ... Na are known only in a few cases. The case parallel to the present one, viz., L_15L_2 is obtained in the spectra of O, Fl^+ and Ne^{++} . The actual $^1P-^3P$ separations here are unknown, but in Fl^+ , $^3P_0 < ^3P_1 < ^3P_2$. The difference $^1P-^3P$ is best known for the coupling L_1L_2 , and the figures are given below :—

$*5KL_1L_2.$	Be.	B $^+$.	C $^{++}$.
3P		165343	331939
		↖ 44414	↖ 58828
1P		120929	273111

The separation varies as the net charge on the atom.

In other cases as well, for the group $2KL_1XL_2$, the published figures, as far as they are available, support the view that the coupling causes large separation in the value of the terms due to different multiplication, and the value arises roughly as the net nuclear charge.

Element.	Na (11).	Mg (12).	Al (13).	Si (14).	P (15).	S (16).
$^1P-^3P$						
$\frac{R}{Z-\sigma}$	·76	·92	1·04	1·25	—	—
$Z-\sigma$	9	10	11	12	13	14
$\frac{\Delta\nu}{Z-\sigma}$	0·85	·092	·094	·102	—	—

$Z - \sigma$ = net nuclear charge, the two K-electrons being regarded equal to two negative charges and causing a diminution of the central charge by two units.

The mean value of $\Delta\nu = 10318$, and the separations observed in the terms of different multiplicity due to the $L_1 \times L_2$ coupling amongst the neutral atoms is of this order.

My thanks are due to Prof. M. N. Saha, F.R.S., for many helpful suggestions contained in this paper.

University College of Science,
92 Upper Circular Road, Calcutta,
7th Feb., 1929.

LXXXV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 272.]

June 26th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S.,
President, in the Chair.

THE following communications were read:—

1. 'The Geology of the District around Abbey-Cwmhir (Radnorshire).' By Richard Owen Roberts, M.Sc.

This paper deals with an area of about 30 square miles in North-Western Radnorshire, immediately east of the Rhayader district described by Dr. Herbert Lapworth¹. The rocks belong to the Bala, Valentian, and Wenlock Series.

The Bala rocks have been divided into two groups. The lower group consists of black and blue graptolitic shales and mudstones with grit-bands, which may be correlated with the middle part of the Mydrim Shales of South Wales. A dolerite-sill has been intruded into these black shales. On the west, the upper group consists in the lower part of grey-blue coarsely-mottled mudstones, which yield a few shelly fossils near the base; they are followed by dark-blue rusty-weathering shales and mudstones, while the highest Bala rocks exhibit some lateral variation, and consist of sandy mudstones, shales, and grits. The lithological succession in these Upper Bala rocks resembles that described in other areas in Central Wales. On the east, the Upper Bala rocks consist of grey-blue fossiliferous mudstones.

Only the lowest beds of the Birkhill Stage are exposed, and they are overstepped by the Tarannon Stage, which, over most of the

¹ Q. J. G. S. vol. lvi. (1900) p. 67.

area, rests directly on folded Bala rocks. The succession in the Tarannon is most complete on the north-west; but, eastwards, the upper part of the Tarannon overlaps the lower.

The basal beds of the Wenlock Series consist of mudstones and shales, which are followed by thickly-bedded micaceous grits. In certain localities there appears to be a slight unconformity between the Wenlock and the Tarannon.

The Bala rocks are exposed along the north-eastern extension of the Towy Anticline; but, in this district, the anticlinal axis is partly replaced by an important strike-fault, which fades westwards. Subsidiary folds may be recognized within the Bala rocks. The axes of these folds are parallel to the general strike of the strata, although there is a change in the direction of pitch around Nantmel. The Bala rocks were folded in pre-Tarannon times, but broad shallow folds in the Tarannon and Wenlock rocks indicate that there has been a repetition of folding along the same lines at different periods.

2. 'The Geology of the Country around Bodfean (South-Western Carnarvonshire).' By Charles Alfred Matley, D.Sc., F.G.S., and Albert Heard, Ph.D., M.Sc., F.G.S.

The authors describe the geology of a tract of country, about $3\frac{1}{2}$ miles long by 2 miles wide, between Nevin and Pwllheli, chiefly in the parish of Bodfean. It includes the prominent hill of Garn Bodfean (918 feet above O.D.) and a lesser hill, Moel y Penmaen. Most of the remaining ground is covered by drift.

The country can be divided into two belts with reference to the dominant east-north-easterly strike. The northern belt includes Garn Bodfean and the ground north of Bod-eilan Mill; the southern belt runs from Glan-y-gors to Penprys, through Bodfean Hall and Moel y Penmaen.

In the southern belt there is a volcanic series of submarine lavas and tuffs interbedded with ashy and argillaceous sediments. Fossils found at several horizons indicate a Lower Bala age. Owing to the high dips, mostly nearly vertical, a great thickness (some 3000 feet) of rocks is present in this belt. There is no folding, but there is some strike- and dip-faulting. A zone of tuffs of intermediate composition south of Bodfean Hall is 1000 feet or more thick. The lavas are closely allied to the so-called spilitic suite, and include oligoclase-keratophyres, augite-andesites, and a pyroxene soda-trachyte which may be an albitized augite-andesite.

Garn Bodfean, in the northern belt, has received previous attention from several geologists, and is usually regarded as probably an intrusive boss or neck of andesite. Detailed examination shows that it consists of a great mass of 'felted' and granular keratophyres and some quartz-keratophyres. The 'felted' keratophyres on the southern margin of the hill are seen in a quarry to overlie, at angles of 60° to 70° , a group of bedded tuffs and

agglomerates, the latter resting in turn upon a flow of hypersthene-andesite. Except on this side of the hill, the keratophyres are surrounded everywhere by the Nevin Shales, which have not yielded fossils, but are probably of Llanvirnian age. The curved boundary between the keratophyres and the shales on the western side has been proved by an excavation to be a thrust-plane of low hade, and it is possible that the junction on the northern and eastern flanks may be of the same nature. Keratophyres and quartz-keratophyres, closely akin to those of Garn Bodfean, occur again in the eastern part of the area, north of Bod-eilan Mill, and they are present in force in the country on the north. It seems, therefore, very possible that the whole hill is a transported mass carried over the Nevin Shales by earth-movements.

All the igneous rocks of the area are considered to be extrusive, with the possible exception of a basalt which may be a sill. A detailed account of the petrography is given, with several new chemical analyses.

The paper discusses the tectonics of the area, the Bodfean volcanic series of the southern belt being regarded as part of the volcanic series of Llanbedrog and Madryn brought up as a fold, and the Garn Bodfean Thrust being compared with the Penmorfa Thrust near Criccieth and the deformed thrust of St. Tudwal's Peninsula.

3. 'The Petrography of the Borrowdale Volcanic Series of the Kentmere Area (Westmorland).' By George Hoole Mitchell, Ph.D., M.Sc., F.G.S.

In a previous communication the succession and structure of the Borrowdale Volcanic Series in Troutbeck, Kentmere, and Long Sleddale were described. The present paper forms the sequel, and deals with the petrography of the rocks of that area. The volcanic rocks are composed of both lava-flows and tuffs, and chemical analyses and microscopical examination show them to be of intermediate composition, varying from basic andesites to rhyolites. The rocks are greatly altered, and this has led to difficulty in distinguishing between lava-flows and tuff-deposits, particularly when the former are brecciated owing to flow. The characters of the lava-flows and tuff-deposits are discussed in detail.

The alteration of the rocks, as shown by the changes in mineral composition, together with the materials filling the vesicles, is considered. The conclusion is reached that much of the alteration may be referred to a variety of propylitization.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

